PB86-168291

Sources, Fates and Effects of Aromatic Hydrocarbons in the Alaskan Marine Environment with Recommendations for Monitoring Strategies

Battelle Pacific Northwest Labs., Sequim, WA

Prepared for

Corvallis Environmental Research Lab., OR

Mar 86

U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-168291

EPA/600/3-86/018
March 1986

SOURCES, FATES AND EFFECTS OF AROMATIC HYDROCARBONS IN THE ALASKAN MARINE ENVIRONMENT WITH RECOMMENDATIONS FOR MONITORING STRATEGIES

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Under

Interagency Agreement No. TD 1668
to the U.S. Department of Energy
Richland, Washington 99352

ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CORVALLIS, OR 97333

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NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

230

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA/600/3-86/018

2.

3. RECIPIENT'S ACCESSION NO.

4. TITLE AND SUBTITLE
Sources, Fates and Effects of Aromatic Hydrocarbons in the Alaskan Marine Environment with Recommendations for Monitoring Strategies

5. REPORT DATE
March 1986

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
J.W.Anderson, J.M.Neff, and P.D.Boehm

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Pacific NW laboratory, Sequim, WA 98382 and
Battelle, Duxbury, MA 02332

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
EPA-82-D-X0533

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Research Laboratory
Office of Research and Development
U.S.Environmental Protection Agency
Corvallis, OR 97333

13. TYPE OF REPORT AND PERIOD COVERED
Project Report

14. SPONSORING AGENCY CODE
EPA 600/02

15. SUPPLEMENTARY NOTES
1985. Project Officer: James C. McCarty FTS 420-4601

16. ABSTRACT

Information about polycyclic aromatic hydrocarbons in the Alaskan marine environment is relatively sparse. About 300 references were reviewed to create an assessment of the current state of knowledge on sources, fates and effects of oil-derived polycyclic aromatic hydrocarbons in cold marine waters.

The objective of this report is to critically review what is known about the sources, fates and effects of polycyclic aromatic hydrocarbons (PAH) in the Alaskan marine environment. Based on this review several information needs are identified and recommendations made for the design of research and monitoring strategies to fill these needs.

The specific areas reviewed are 1) the natural and anthropogenic sources fo aromatic hydrocarbons in the Alaskan marine environment, 2) the physical, chemical and biochemical fates of these compounds in marine ecosystems, and 3) the bioaccumulation and biological effects of aromatic hydrocarbons in marine organisms.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT
Release to Public

19. SECURITY CLASS (This Report)
Unclassified

20. SECURITY CLASS (This page)
Unclassified

21. NO. OF PAGES
132

22. PRICE

EPA Form 2220-1 (9-73)

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under EPA-82-D-X0533 to Pacific Northwest Laboratory. It has been subject to the Agency's peer and administrative review and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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ACKNOWLEDGMENT

The authors are grateful to the U. S. Environmental Protection Agency for the funding required to prepare this document. We appreciate the constructive comments of outside reviewers and those of our colleague, Dr. James States in our Anchorage office. Thanks also go to Jan Engel and Joan Pfeifer for the preparation of the manuscript and illustrations.

SOURCES, FATES AND EFFECTS OF AROMATIC HYDROCARBONS IN THE ALASKAN MARINE ENVIRONMENT WITH RECOMMENDATIONS FOR MONITORING STRATEGIES

1. INTRODUCTION

Representatives from 19 Federal and state agencies met in 1982 to prioritize 17 problems being considered for funding by the Cold-Climate Environmental Research Program of the U.S. Environmental Protection Agency. Ranked fourth in importance was the need for an overview of the current state of knowledge on fate and effects of oil-derived hydrocarbons in cold marine waters. Although a moderate amount of research has been done in this area, many of the results have not yet been published or if published, have been in obscure journals and the so-called "grey" literature. There was a need to collect the most relevant literature and present it from the viewpoint of professionals in the field as a basis for determining the future directions of research.

The importance of such an effort was underscored by Battelle Memorial Institute's working session on "The Determination of Unreasonable Environmental Degradation in Alaskan Marine Waters" held in Anchorage, Alaska during March of 1984. Approximately 30 key individuals active in offshore oil development were invited from the oil industry, state and Federal agencies and other interested organizations to seek ways of resolving current impasses.

The transport, fate and effects of petroleum-derived hydrocarbons, particularly aromatic hydrocarbons that might be released in discharges of produced waters (PW), was a major topic of discussion. Participants were asked to develop lists of useful things to do and, using a computer-assisted process, rank them from most to least useful. Among the agency and industry representatives there was remarkable consensus. From a list of 31 useful things to do, 8 of the 9 identified as most useful and 8 of the 10 identified as least useful by industry were so identified by the agencies as well. On the other hand, the limited native representation ranked the priorities almost the reverse. For example, items ranked 1 and 6 from the native perspective were ranked 24 and 31 by the agencies and industry. The need for more extensive dialogue between industry and Federal/state agencies on one hand and native organizations on the other was one of the important conclusions of the working session.

The PW activities seen as most useful by the agencies and industry were to:

(1) Develop a management decision framework for PW discharges and the criteria to be applied in its use.

(2) Determine the behavior of PW discharge plumes and sedimentation of contaminants from plumes, including the evaluation and verification of existing dispersion models.

(3) Evaluate acute toxicity of components from PW discharges where the toxicity of the components is not already known.

(4) Identify areas of high potential for contaminant persistence and impacts from PW discharges.

(5) Evaluate potential chronic effects of components from PW discharges.

(6) Examine the feasibility and consequences of alternatives to PW discharge to the ocean.

The objective of this report is to critically review what is known about the sources, fates, and effects of polycyclic aromatic hydrocarbons (PAH) in the Alaskan marine environment. Based on this review, we identify several information needs and recommend the design of research and monitoring strategies to fill these needs.

While a considerable amount of information has been generated regarding the fates and effects of petroleum components, there are untested conditions and unique areas in the Alaskan marine environment that require special consideration. It is important to first bring to light the findings in these research areas that are relevant to Alaskan conditions and then to identify gaps in our understanding which require further experimentation.

First, we will examine the natural and anthropogenic sources of aromatic hydrocarbons in the Alaskan marine environment. Then we will review the physical, chemical, and biochemical fates of these compounds in marine ecosystems. Finally we will review the current knowledge on the bioaccumulation and biological effects of aromatic hydrocarbons in marine organisms. Based on this review, we will make recommendations concerning research needed to better understand the processes affecting aromatic hydrocarbons in the Alaskan marine environment.

Since its inception in 1975 through an interagency agreement between the Department of the Interior, Bureau of Land Management (now Minerals Management Service) and the Department of Commerce, National Oceanic and Atmospheric Administration, the Outer Continental Shelf Environmental Assessment Program (OCSEAP) has provided financial support and technical guidance for a very large number of investigations dealing with all aspects of the impacts of oil and gas exploration and development on the Alaskan marine environment. A recent comprehensive bibliography (OCSEAP, 1984) lists titles of more than 3,000 documents dealing with research supported by OCSEAP. We have made extensive use of these documents in preparing this review, particularly those documents in the form of final reports and publications in the hard literature.

2. SOURCES OF AROMATIC HYDROCARBONS IN THE ALASKAN MARINE ENVIRONMENT

Polycyclic aromatic hydrocarbons (PAH) may be formed by a variety of mechanisms. These include the very rapid, high temperature (e.g., 700°C) incomplete combustion or pyrolysis of organic materials, the very slow (e.g., millions of years) rearrangement and transformation of organic materials at moderate temperatures of 100-300°C to form fossil fuels, the relatively rapid (days-years) transformation of certain classes of organic compounds in soils and sediments, and possibly biosynthesis.

BIOSYNTHESIS

It is well-known that a wide variety of organic molecules containing fused-ring polyaromatic systems are synthesized by organisms, particularly bacteria, fungi, and higher plants. Many of these compounds are not true PAH's since they contain oxygen, nitrogen or sulfur substituents. For example, microorganisms, higher plants, and even a few animals synthesize a wide variety of polycyclic quinone pigments. Vitamin K_2 is a naphthoquinone. The marine marsh grass *Juncus roemerianus* synthesizes large amounts of a pigment called juncusol which is a phenanthrene quinone.

Under oxygen-free conditions, as occur in many marine and freshwater sediments, these quinones and phenols may be reduced to the parent PAH. A four-ring PAH, perylene, frequently occurs at high concentrations in anaerobic freshwater and marine sediments (Aizenshtat, 1973; Gschwend et al., 1983; Louda and Baker, 1984).

It is thought that perylene is formed in anoxic sediments by the reduction of extended quinone pigments synthesized by fungi and other microoganisms living at the sediment/water interface. Under oxidizing conditions, certain chemicals such as abietic acid from pine tree resin and triterpenes (hopanes) from mosses and certain other plants can be oxidized to PAH (Tan and Heit, 1981). Retene (methyl-isopropyl phenanthrene) is a common PAH found in coniferous forest soils. The PAH assemblages produced by the early diagenesis of suitable biogenic precursors will have a simple composition.

All attempts to date to demonstrate the direct biosynthesis of PAH by bacteria, algae and higher plants have yielded negative or equivocal results (see review by Neff, 1979). If direct biosynthesis of PAH does occur, it is of minor importance in the overall mass loading of PAH in the environment.

FOSSIL FUELS

Transformations similar to those described above for the early diagenic formation of perylene and alkyl phenanthrenes, if allowed to continue for millions of years under the right temperature and pressure regimes, lead to the formation of fossil fuels containing a great diversity of hydrocarbons, including PAH.

Coal generally is considered an aromatic material. Most of the PAH in coal are tightly bound in the coal structure and cannot be leached out. Total PAH concentrations tend to be higher in hard coal than in soft coals, like lignite and brown coal. However peat deposits prevalent over vast areas of the arctic tundra, may contain high concentrations of some PAH, particularly perylene.

Crude petroleum, shale oil and most refined and residual petroleum products are extremely complex mixtures of many thousands of organic compounds. Typical crude petroleums may contain from 0.2 to more than 7 percent PAH. Kerosene, gasoline, and diesel oil contain relatively low concentrations of tricyclic and larger PAH, while heavy oil products such as Bunker C oil (residual oil) and asphalt may contain several percent PAH (Neff, 1979). Shale oil and coal-derived synthetic crude oils may contain as much as 15 percent PAH.

The four API reference oils have been used extensively in biological effects studies and considerable information is available about their chemical composition (Anderson et al., 1974a; Pancirov and Brown, 1975). Concentrations of several PAH in these oils are listed in Table 1. Most oils contain the same hydrocarbons, but the relative proportions of different hydrocarbons vary widely from one oil to another. Nearly always, alkyl homologues are present at higher concentrations in crude and refined oils than are the parent PAH (Blumer, 1976). This is reflected in the relative concentrations of naphthalene and C_1-C_3 naphthalenes in the four API oils.

Benzo(a)pyrene (BaP) often is used as a marker or indicator of the presence of carcinogenic PAH in environmental samples. Typical concentrations of BaP in crude, refined and residual oils and coal are summarized in Table 2. Crude petroleum and products refined from crude petroleum generally contain low concentrations of BaP. Shale oil and coal-derived oils contain substantially higher concentrations. Residual oils and coal contain intermediate amounts. Concentration of BaP in motor oil increases during usage through pyrolysis.

PYROLYSIS

A majority of PAH in the environment is formed during the incomplete combustion of organic matter at high temperatures (Suess, 1976). When heated to high temperature, organic molecules are broken into smaller fragments (pyrolysis) which then are rearranged into different configurations, including PAH (pyrosynthesis), as they cool. Optimal conditions for PAH pyrosynthesis include a fuel-rich flame (high fuel to air

TABLE 1. CONCENTRATIONS OF PAH IN TWO CRUDE OILS AND TWO REFINED OILS

Compound	Concentration in mg/kg (ppm)			
	South Louisiana Crude	Kuwait Crude	No. 2 Fuel Oil	Bunker C Residual Oil
Naphthalene	400	400	4000	1000
1-methylnaphthalene	800	500	8200	2800
2-methylnaphthalene	900	700	18900	4700
Dimethylnaphthalenes	3600	2000	31100	12300
Trimethylnaphthalenes	2400	1900	18400	8800
Fluorenes	200	<100	3600	2400
Phenanthrene	70	26	429	482
1-methylphenanthrene	111	-	173	43
2-methylphenanthrene	144	89	7677	828
Fluoranthene	5.0	2.9	37	240
Pyrene	3.5	4.5	41	23
Benz(a)anthracene	1.7	2.3	1.2	90
Chrysene	17.56	6.9	2.2	196
Triphenylene	10	2.8	1.4	31
Benzo(ghi)fluoranthene	1	<1		
Benzo(b)fluoranthene	<0.5	<1		
Benzo(j)fluoranthene	<0.9	<1		
Benzo(k)fluoranthene	<1.3	<1		
Benzo(a)pyrene	0.75	2.8	0.6	44
Benzo(e)pyrene	2.5	0.5	0.1	10
Perylene	34.8	<0.1	-	22
Benzo(ghi)perylene	1.6	<1		

TABLE 2. TYPICAL CONCENTRATIONS OR CONCENTRATION RANGES OF THE PAH CARCINOGEN BENZO(a)PYRENE(BaP), IN PETROLEUM AND COAL PRODUCTS

Material	BaP Concentration Range mg/kg (ppm)
Crude Petroleum	0.10-3.6
Shale Oil	10-30
Diesel Fuel	0.2-0.7
No. 2 Heating Oils	0.01-0.05
Gasoline	0.03-6.2
Motor Oils (new)	0.06-0.25
Motor Oils (used)	0.07-35
No. 4 Residual Fuel Oil	2.1
No. 5 Residual Fuel Oil	2.8-3.3
No. 6 Residual Fuel Oil (Bunker C)	26-44
Asphalt	0.1-27
Coal-Derived Oils	1.3-180
Bituminous Coal	6-20

ratio) and a flame temperature above about 500°C. Nearly all of the airborne PAH produced by flame pyrolysis are associated with the particulate fraction produced during combustion (soots and carbon blacks).

Unlike PAH assemblages in fossil fuels, PAH assemblages formed by pyrolysis are dominated by the parent compound with a decreasing frequency of PAH homologues with increasing numbers of alkyl carbons. These differences between composition of PAH assemblages in fossil fuels and combustion sources may be used to aid in the identification of the sources of PAH in environmental samples.

A great many domestic and industrial activities involve pyrosynthesis of PAH. The resulting PAH may be released to the environment in airborne particulates or in solid or liquid by-products of the pyrolytic process. Domestic activities that produce significant quantities of PAH include cigarette smoking, home heating with wood or fossil fuels, waste incineration, broiling and smoking of foods, and use of internal combustion engines. Many industrial activities produce large quantities of PAH. These include coal coking; production of carbon blacks, creosote, coal tar and related materials from fossil fuels; petroleum refining; synfuel production from coal; and use of Soderberg electrodes in aluminum smelters and iron works, etc. (Neff, 1979).

The burning of various fuels as a source of heat or energy is one of the most important sources of PAH in the environment (Table 3). The particulate fraction of the exhaust from gasoline and diesel engines contains high concentrations of one to six-ring PAH (Stenberg et al., 1983). Modern fossil fuel power plants and municipal waste incinerators emit relatively small amounts of PAH in stack gases or fly ash per unit fuel burned. However, because of the large amounts of fuel or waste burned, mass emission rates may be quite high.

Home heating with wood, coal and peat in stoves, fireplaces or hot water boilers, which is common in rural and even many residential areas in Alaska, results in the emission of relatively large amounts of PAH in smoke. Domestic wood-burning stoves produce the greatest PAH emissions, particularly when the fire is banked or allowed to smolder. Air pollution associated with use of wood- and coal-fired stoves for home heating has risen to the point that this type of heating has been prohibited in parts of several cities in Canada and Alaska, including Juneau. Forest fires and open burning of brush and plant wastes are also important sources of particulate emissions rich in PAH. Sullivan and Mix (1983) estimated that as much as 1.3 kg of total PAH were generated per hectare during slash burning of clear-cut logging sites in Oregon.

Solid wastes (ash and creosote) from coal and wood burning also contain significant concentrations of PAH. The relative importance of stack gas, ash, and creosote as sources of PAH depends on the ratio of stack gas to ash produced during combustion, which in turn depends on the type of wood or coal burned, and the combustion conditions.

TABLE 3. TYPICAL CONCENTRATIONS OF BENZO(a)PYRENE AND TOTAL PAH IN GASEOUS AND PARTICULATE EMISSIONS FROM BURNING OF DIFFERENT FUELS *

Fuel	Emission Rate (mg/kg fuel burned)	
	Benzo(a)pyrene	Total PAH
Coal, Power Plant (Modern)	4×10^{-5}-0.002	<0.025
Oil, Power Plant	7×10^{-7}-1.5×10^{-5}	<0.04
Refuse, Municipal Incinerator	4×10^{-5}	0.009
Gasoline, Automobile, Noncatalytic	0.016	-
Gasoline, Automobile, Catalytic	4×10^{-4}	-
Coal, Residential Stove	25	-
Wood, Residential Stove	0.05-6.5	2.6-250
Charcoal, Residential Stove	3.3×10^{-4}	0.095
Wood, Residential Hot Water Boiler	0.02	1.94
Peat, Residential Hot Water Boiler	0.06	14.9
Wood, Residential Fireplace	0.005-1.9	-
Brush, Open Slash Burning	2-12	75-176

*Data from Davies et al., 1976; Alsberg and Stenberg, 1979; Dasch, 1982; Ramdahl et al., 1982; Ahlberg et al, 1983; Sullivan and Mix, 1983; Knight et al, 1983.

Many industrial processes produce by-products or effluents rich in PAH. The best known is the production of coke from coal. Coke is an important high-energy fuel used extensively by the iron and steel industry. The particulate fraction of stack gases from a coking oven may contain up to five percent PAH (Lao et al., 1975).

Catalytic cracking of crude petroleum fractions to produce hydrocarbon fuels and other refined petroleum products results in the production of PAH. These tend to become concentrated in the heavy residual fractions, Bunker C or No. 6 fuel oil and asphalts. Significant quantities of PAH may be released in flue gases and in waste water effluents. Most of the PAH are removed by various methods before the waste streams are released to the environment. The treated flue gas from an oil refinery may contain 1-10 ug total PAH/m^3 (Sawicki et al., 1965).

Activated sludge treatment of liquid waste effluents from oil refineries removes up to 95 percent of the five-ring PAH and more than 99 percent of the four-ring PAH (Pancirov et al., 1980). However, the small amount of PAH remaining in the effluent includes known carcinogens (e.g., methyl- and dimethyl benzanthracene, and benzo(a)pyrene). Jensen (1983) reported that a refinery effluent discharged to a Danish estuary contained an average of 0.08 parts per billion benzo(a)pyrene. Sediments and mussels (Mytilus edulis) from the estuary contained 27-54 ppb and 5-87 ppb, respectively of benzo(a)pyrene.

Several metal-smelting processes produce gaseous and liquid waste streams rich in PAH. Soderberg electrodes are sometimes used in aluminum smelters, ferrosilenium and iron works, and calcium carbide production. Soderberg electrodes are made of anthracite coal, coke tar, pitch and anthracene oil. During metal smelting the electrode is burned continuously and the high boiling PAH escape in the fumes (Palmork et al., 1973). The production of one ton of aluminum consumes half a ton of electrode material. Particulate PAH may escape to the environment in the flue gas, in water effluent from the gas scrubber system, or in the sludge resulting from treatment and recycling of the scrubber water. Bjorseth and Eklund (1979) identified more than 100 PAH and related heterocyclic compounds in the working atmosphere of an aluminum smelter. Palmork et al. (1973) identified and quantified several PAH in waste water and sludge effluents from Norwegian aluminum smelters and in bottom sediments and associated benthic biota from the fjords into which effluents were discharged. The scrubber sludge contained about 700 mg/kg (ppm) low molecular weight PAH (anthrace-pyrene). Contaminated fjord sediments contained more than 1700 ppm of these compounds.

There are, of course, many other natural and anthropogenic sources of PAH. The extreme diversity of sources of environmental PAH and our limited knowledge about them makes any estimate of the global flux of these organic molecules very difficult.

RATES AND ROUTES OF ENTRY OF PAH INTO THE MARINE ENVIRONMENT

PAH formed by the processes discussed above may reach marine and freshwater environments by a wide variety of routes. Major routes of entry of PAH to marine waters include early diagenesis of suitable precursors, spillage and seepage of fossil fuels, discharge of industrial and domestic waste water, fallout or washout in precipitation from air, and runoff from land.

In situ formation of PAH will be restricted to sediments of anoxic basins or other restricted environments and is unlikely to contribute significantly to the overall mass loading of PAH in Alaskan coastal waters and sediments. However, peat moss, as indicated above, can contain high concentrations of certain early diagenic PAH (i.e., perylene and retene). There are extensive deposits of tundra peat in northern and interior Alaska (Schell, 1983). Riverine and coastal erosion results in substantial inputs of this material to Alaskan coastal waters. It has been estimated that coastal erosion alone results in the introduction of 700 metric tons of peat per km of coast per year to the Alaskan Beaufort Sea. Major rivers such as the MacKenzie and Yukon also introduce massive amounts of peat to coastal waters.

Spillage and seepage or erosion of fossil fuels into the ocean is an important source of PAH in this environment. World oil production was estimated at about 3,100 million metric tons in 1981 (Miller and Connell, 1982). These authors estimated that from 4.5 to 6.1 million tons of petroleum (0.15-0.20% of production) enters the marine environment each year. Since crude and refined oils may contain up to several percent total PAH, this accidental spillage and natural seepage represents a quantitatively important input of PAH to the marine environment. Erosion or disposal of coal or coal dust also may be an important source of PAH in coastal environments (Tripp et al., 1981).

Blasko (1976) described 18 oil and 7 tar seep areas in the northern Gulf of Alaska. There are gas seeps in Norton Sound near Nome (Cline and Holmes, 1977), and in the southern Bering Sea near the Pribilof Islands (Kvenvolden and Ridden, 1980). There are coal outcrops along the Mead River and an oil seep area near Smith Bay in the Alaskan Beaufort Sea (Shaw et al., 1979). The MacKenzie River drains the Athabasca tar sands and Normal Wells seep area of north-central Canada and discharges to the Beaufort Sea a short distance west (up-current) of the Alaskan border. These natural seeps or erosional sources may contribute significantly to PAH assemblages detected in Alaskan coastal sediments (Shaw et al., 1979; Stich and Dunn, 1980; Atlas et al., 1983).

Two activities associated with oil production and transport in Alaska which result in the discharge of large amounts of hydrocarbon-contaminated waste water are produced water production and ballast water treatment. Most petroleum reservoirs also contain fossil water. When the oil is removed from the formation, some of this water, called produced water or oilfield brine water, comes with it (Neff, 1985). This produced water usually has a salt concentration as high as or higher than that of seawater and also contains high concentrations of petroleum hydrocarbons. The produced water may be reinjected through another well back into the reservoir or it may be treated to remove particulate oil and discharged to the surface. Although some produced water may reach arctic wetland tundra and coastal areas via its discharge into reserve pits and subsequent discharge or leaching, the only place in Alaska where treated produced water currently is discharged directly to the marine environment is in Cook Inlet. Lysyj (1982) estimated that in 1982 an average total of 12.9 million liters per day of produced water was discharged to Cook Inlet from two on-shore treatment plants (at Kenai and Trading Bay) and from one offshore production platform (Dillon).

There are several discharges of produced water to Cook Inlet other than those studied by Lysyj. These include a treatment plant at Granite Point, and platforms Anna, Bruce, Baker, and the Phillips A gas platform. Thus, the rate of produced water discharge to Cook Inlet is substantially greater than the 12.9 million liters/day reported by Lysyj (1982). A reasonable estimate would be twice as much or 25.8 million liters/day. The treated produced water effluent contained 5.8 to 42 ppm particulate oil (mean 21 ppm) and an average of 10 ppm volatile monocyclic aromatic hydrocarbons (benzene, toluene, xylene). Unfortunately, Lysyj (1982) did not measure concentrations of PAH in the produced water effluent. Armstrong et al., (1979) reported that a produced water sample from the Texas coast, containing about 10 ppm monoaromatics, contained a total of 1.74 ppm two- and three-ring aromatics. If we used a value of 1.5 ppm as an average concentration of lower molecular weight PAH in produced water, then a total of 38.7 kg/day or 14.1 metric tons/year of low molecular weight PAH are released to Cook Inlet with about 826 metric tons/year of total petroleum hydrocarbons in produced water. Whereas reinjection often is a feasible alternative to surface discharge in on-land oil fields, this usually is not the case for offshore fields. Therefore, if or when oil production occurs in the Beaufort and Bering Seas, there may be a need to discharge treated produced water to these water bodies. The current permit for development of the Endicott Field in the Beaufort Sea calls for reinjection of produced water.

Crude oil tankers arrive in ballast at Valdez to take on oil from the southern terminus of the trans-Alaska pipeline. The tankers discharge their ballast water to a treatment facility before taking on oil cargo. The Valdez ballast water treatment facility discharged a total of 33.4 billion liters of treated ballast water, containing an estimated 132 metric tons of particulate oil and 170 metric tons of volatile hydrocarbons (mainly benzenes) during the first two years of operation, August 1977-July 1979 (Lysyj et al., 1981). The effluent probably contained no more than 0.25 ppm of low molecular weight PAH (Rice et al., 1981). Based on these figures, approximately 4.2 metric tons/year of low molecular weight PAH were discharged to Valdez Harbor in treated ballast water.

A massive oil spill may result in the introduction of massive amounts of PAH within a relatively small area. For instance, approximately 250,000 metric tons of crude oil was released and spread to approximately 350 km of the Brittany coast of France after the Amoco Cadiz spill. If this oil contained two percent total PAH, a total of 5,000 metric tons of PAH was released to the marine environment within a few days. There have been no major oil spills in Alaskan coastal waters. However, small spills (less than 50 barrels: 7,900 liters), do occur occasionally during normal tanker and offshore production platform operations. Should development occur in the Norton Sound, Navarin, North Aleutian or St. Georges Basin areas of the Bering Sea or in the Chukchi Sea, the produced oil probably would be transported to refineries via tankers, increasing the likelihood of spills from this source.

Industrial and domestic sewage often contains high concentrations of particulate and soluble PAH. Several of the industrial sources of these PAH were discussed above. Storm sewage (runoff from roadways, etc.) contains PAH arising from wear and leaching of asphalt road surfaces, wear of vehicle tires which contain carbon black, condensation from vehicular exhaust, and from the all too common practice in Alaska and elsewhere of oiling roadsides and unpaved roadways with used crankcase oil (high in PAH). Several investigators have identified used crankcase oil as a major source of PAH in stormwater runoff from urban and rural areas (Hoffman et al., 1984).

Treated and sometimes untreated liquid sewage is nearly always discharged to any available water body (river, lake, estuary). Solid residues from activated sludge treatment of wastes may be disposed of in the ocean or in land fills. Liquid dometic sewage usually contains less than 1 ug/liter total PAH, industrial sewage from 5 to 15 ug/liter PAH, and sewage sludge from 1 to 30 mg/kg (Neff, 1979).

Most of the PAH emitted to the atmosphere during the burning of organic matter are adsorbed to microscopic particles (Suess, 1976). Atmospheric processes that result in the deposition of airborne PAH on land and water include washout in precipitation, dry fallout and vapor phase deposition onto surfaces. For many years it was assumed that airborne particulate PAH were degraded rapidly by photooxidation processes (NAS, 1972). There is growing evidence, however, that airborne particulate PAH may be transported in environmentally significant concentrations over thousands of kilometers (Lunde and Bjorseth, 1977; Bjorseth et al., 1979).

There has been growing interest in recent years in the source and composition of seasonal atmospheric haze that occurs throughout much of the Arctic each year. This haze, called the Arctic aerosol, contains relatively high concentrations of several pollutant metals (Heidam, 1984) as well as organic pollutants, including PAH (Daisey et al., 1981). The concentration of pollutants in the Arctic aerosol is highest in the winter. The pollutants are thought to come from major industrial sources in the middle latitudes (i.e., the central U.S., Europe, China and Russia). At Point Barrow, the mean concentration of total PAH was 1.25 ug/m^3 in March and 0.14 ug/m^3 in August (Daisey et al., 1981).

The March samples contained fly ash particles, suggesting industrial coal and oil burning as as source of the PAH. In August, the PAH profile resembled that of vehicular exhaust particulates, probably of local origin. The concentrations of PAH in the Arctic aerosol at Point Barrow, Alaska, are similar to those in other remote atmospheres, and much lower than concentrations typically reported for urban atmospheres (e.g., 6-9 ug/m^3 in New York: Daisey et al., 1981, and 2.9-155 ug/m^3 in Fairbanks, Alaska: Reichardt and Reidy, 1980). Shaw et al. (1979) suggested that long-range transport of air-borne particulates from mid-latitude industrial sources was a major source of PAH in coastal sediments of the Alaskan Beaufort Sea.

The estimated annual input of PAH to the marine environment from the sources discussed above is approximately 230,000 metric tons total PAH/year (Neff, 1979). Surface runoff from land and fallout from the air appear to be the main sources of high molecular weight PAH in the marine environment, while petroleum seepage and spillage is the main source of total PAH. This reflects the relatively high PAH content (mainly bi- and tri-cycle PAH) of petroleum in comparison to other major PAH sources.

ALASKAN PERSPECTIVE

Although several point sources of polycyclic aromatic hydrocarbons in the Alaskan marine environment have been identified (i.e., produced water and ballast water discharges), these probably do not contribute more than a small fraction of the total PAH entering Alaskan coastal waters from all sources. In non-industrial areas of the world, including most of Alaska, major sources of PAH in coastal waters and sediments are from aerial deposition of particle-associated PAH derived from remote industrial and other combustion sources (Neff, 1979; Hites et al., 1980; Johnson et al., 1985). In Alaska, wood burning for home heating and in controlled or wild forest fires are major sources of airborne PAH which may eventually reach the marine environment. Erosion of peat and coal deposits probably are major sources also, particularly to the Beaufort and Bering Seas.

3. FATE OF OIL SPILLS AND CHRONIC EFFLUENTS

In the past twenty years there have been many massive spills of crude, refined and residual petroleum products to the marine environment as a result of oil tanker accidents and blowouts on offshore oil platforms. Following the peak years of 1978 (Amoco Cadiz Oil Spill) and 1979 (IXTOC I blowout) the amount of oil spilled annually in the ocean had declined until 1983, when it rose again (by 9-fold over 1982) to approximately 242 million gallons (912 million liters) (OSIR, 1984). The large increase in oil spilled in 1983 was due to oil well blowouts in the Arabian Gulf as a result of the Iran-Iraq war, and six tanker accidents, each involving loss of 1 million gallons or more of oil. There were no major reported spills (more than 10,000 gallons: 37,854 liters) in Alaska in 1983. Between 1971 and 1980, the average rate of spillage of oil in Lower Cook Inlet was 0.0001 percent of the total crude oil produced (Wondzell, 1981), which is a considerably better record than that for the Gulf of Mexico.

THE GEOCHEMICAL ENVIRONMENT

Several recent studies have documented the distribution of hydrocarbons and metals in Beaufort Sea sediments (Shaw et al., 1979; Kaplan and Venkatesan, 1981; Venkatesan and Kaplan, 1982; Naidu et al. 1981; Burrell et al. 1981). Shaw et al. (1979) examined the hydrocarbon geochemistry of nearshore sediment along a transect from Point Barrow to Barter Island. Total hydrocarbon concentration in the nearshore ranged between 0.3 and 20 μg/g dry sediment. The saturated hydrocarbons were dominated by n-alkanes ranging in chain length from 23 to 31 carbon atoms with a strong odd-even preference and no unresolved complex mixture (UCM) evident. This distribution is consistent with a prevalent biogenic input of terrigenous plant material, most likely resulting from transport of riverine suspended particulate matter during the spring runoff. Shaw et al., also examined sources of aromatic hydrocarbons in nearshore sediments using the alkyl homolog distribution of selected aromatic hydrocarbon series determined by GC/MS. Distributions characteristic of both pyrogenic and petrogenic origins were observed. The geographic distribution of pyrogenic combustion products was indicative of difuse non-point source inputs (probably aerial deposition of particulate PAH), rather than point source inputs. Their analysis also ruled out natural seepage or spills of Prudhoe Bay crude oil as the source of aromatic hydrocarbons in the region.

The hydrocarbon geochemistry of the Beaufort Sea outer continent shelf (OCS) has been studied by Kaplan and Venkatesan (1981) and Venkatesan and Kaplan (1982). The range of total hydrocarbon concentrations reported was 20-50 μg/g dry sediment, which is slightly greater than that found in the nearshore sediments. Whether these differences are due to differences in the analytical methods employed or to a greater abundance of fine-grained, organic-rich sediments in the OCS region was not investigated. As with the nearshore sediments, the major source of saturated sedimentary hydrocarbons was found to be higher plant debris, with no evidence of a UCM indicative of anthropogenic inputs. A marine biogenic origin for some of the organic matter was also indicated by the occurrence of the hydrocarbons pristane and n-heptadecane. The occurrence of several alkanes, together with steranes, diterpanes and triterpanes also attested to the biogenic origin of the organic matter. Measurable concentrations of aromatic hydrocarbons were found in almost all the Beaufort Sea OCS sediments examined. The distribution of alkylated homologues determined by GC/MS was found to be characteristic of pyrogenic origin. Thus, the available organic geochemical data for the region indicate that hydrocarbons found in nearshore and offshore sediments originate primarily through natural processes, with little evidence of anthropogenic petroleum inputs.

Data on the concentrations of hydrocarbons in bivalves from the region are sparse. Shaw et al. (1981) reported very low levels of hydrocarbons in bivalves from the area.

FATE OF OIL IN THE ARCTIC ENVIRONMENT

General Considerations

Although there have been few actual case studies concerning oil spills in Alaskan waters, many of the studies conducted in sub-Arctic and temperate marine environments have provided information which is directly applicable to addressing the fate of oil spilled in Alaskan waters, and on the fate of polycyclic aromatic hydrocarbons in petroleum.

There has been a large number of studies of the fate of spilled oil. The oil spills for which major fate and effects studies were performed during the last two decades are summarized in Table 4. In addition, there have been several investigations of the marine environmental fate and effects of chronic low-level discharges from point sources (e.g. produced water effluents, ballast water effluents, oil-base drilling fluid cuttings discharges, refinery effluents, etc). These studies have demonstrated that PAH from petroleum may be quite persistent in some marine environments and may produce massive immediate biological damage as well as long-term impacts in some low-energy depositional marine environments.

The fate of oil spilled onto the surface of the water generally can be depicted as in Figure 1. This generalized schematic addresses oil spilled on the water's surface prior to landfall. A variety of processes can act on the oil and partition it into various compartments in the marine environment (i.e. water column, sediments, biota).

Each of these processes may act differentially on the various components of oil. It is widely recognized that during the initial stages of a spill or a crude oil discharge, the major transport mechanism of oil

TABLE 4. SUMMARY OF THE MAJOR OIL SPILLS FOR WHICH EXTENSIVE POST-SPILL FATE AND EFFECTS STUDIES WERE PERFORMED

Vessel/Platform	Type of Oil Spilled	Date	Location	Volume Oil Spilled	
				Gallons ($\times 10^6$)	Liters ($\times 10^6$)
Tampico Maru	Diesel Fuel	29 Mar., 1957	Baja Calif., Mexico	2.52	9.54
Torrey Canyon	Kuwait Crude	18 Mar., 1967	Lands End, SW England	36.1	137
Florida	Diesel Fuel	16 Sep., 1969	Falmouth, MA	0.588	2.20
Arrow	Bunker C	4 Feb., 1970	Chedabucto Bay, Nova Scotia	4.54	17.2
Metula	Light Arabian Crude	9 Aug., 1974	Strait of Magellan	60.9	231
Argo Merchant	Bunker C	15 Dec., 1976	Nantucket Shoals, MA	7.67	29.0
Tsesis	No. 5 Fuel Oil	26 Oct., 1977	Swedish Archapelago, Baltic	0.388	1.47
Amoco Cadiz	Iranian & Arabian Crude	16-17 Mar., 1978	Brittany, France	67.2	255
Chevron Block 41 Blowout	Light Crude	10 Feb-31 Mar., 1970	East of Mississippi Delta	2.7	10.3
Ekofisk Bravo Blowout	North Sea Crude	22-30 Apr., 1977	North Sea	6.13	23.2
IXTOC-I Blowout	Mexican Crude	3 Jun., 1979-23 Mar., 1980	Bay of Campeche	139-428	526-1,620

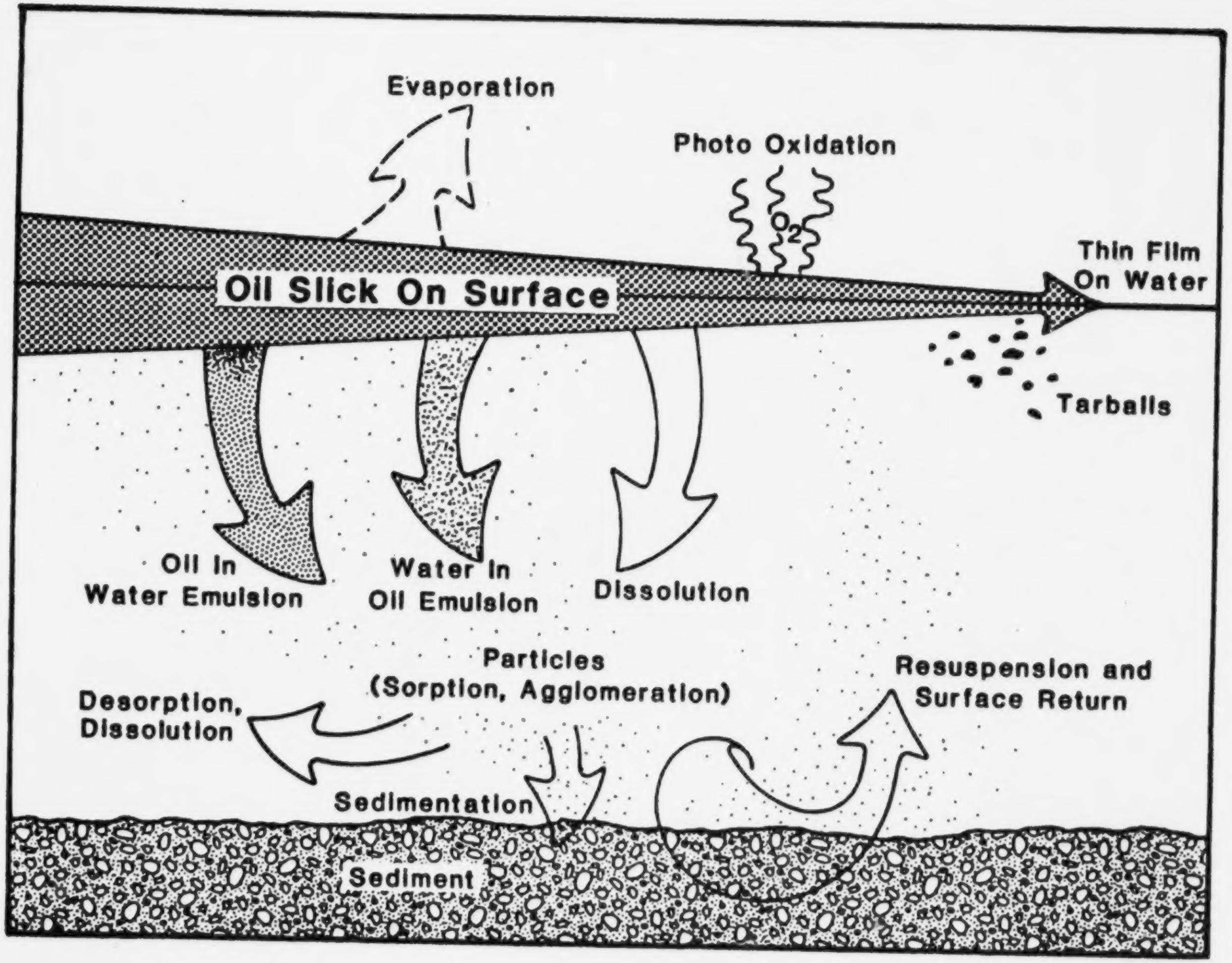

Evaporation
Photo Oxidation
O_2
Thin Film
On Water
Oil Slick On Surface
Tarballs
Oil In
Water Emulsion
Water In
Oil Emulsion
Dissolution
Particles
(Sorption, Agglomeration)
Desorption,
Dissolution
Resuspension and
Surface Return
Sedimentation
Sediment

Figure 1. Transport and interaction path of oil and suspended particulate matter.

into the water column is by physical dispersion. This dispersion results in a spectrum of whole oil droplets in the upper water column. Subsequently, soluble aromatic hydrocarbons, the one- and two-ringed aromatics, preferentially dissolve in the water as a result of the increased surface area of the droplets and due to the relatively high solubility of these aromatic components. As a result, the chemical composition of hydrocarbons in the seawater exclusive of the droplets themselves is distinctly different than that of the whole oil droplets. The water-soluble and more toxic aromatics dominate the dissolved fraction. Animals exposed to the water mass will initially acquire these compounds. However, the total concentration of these dissolved aromatics will seldom exceed 1 ppm and usually is in the 0.01 to 0.1 ppm range. The instantaneous concentration of aromatics and for that matter of the whole oil droplets themselves, is directly dependent on the physical energy of dispersion, i.e., the result of wind and wave induced turbulence.

The worst case of water column exposure is actually represented by either, (1) the subsurface discharge of oil from an oil well blowout (see Brooks, et al., 1981, Boehm and Fiest, 1982) to be discussed below, or by, (2) a chemically dispersed oil plume, also to be discussed below. In these cases, maximum petroleum hydrocarbon levels seldom exceed 50 ppm, with these concentrations rapidly diluted by mixing with seawater by factors of 10^3 to 10^5.

The potentially more serious environmental effects related to petroleum hydrocarbon transport mechnanisms and specifically aromatic hydrocarbons relate to: (1) the sorption of oil droplets on suspended particulate material (SPM) and transport to the bottom; and (2) the landfall or beaching of an oil slick, followed by sorption onto beach sediments and subsequent erosion of these sediments and deposition in the nearshore zone.

Suspended particulate matter interacts with spilled oil through two major processes. The first process which is considered to be quantitively minor is the molecular sorption of dissolved oil species from the water phase onto suspended particles. The second process is the physical collision and adherence of dispersed drops of oil with SPM. The resulting oil-loaded particulate may lose sorbed hydrocarbon components through desorption or microbial biological processes or may ultimately be deposited on and incorporated into the seabed. In Alaska, SPM distributions from riverine runoff and other coastal sources are often highly concentrated in the nearshore zone (Britch, 1976; Barnes and Fox, 1979; Strakov, 1967) and are transported parallel to the coastline. Thus, the sorption efficiencies of SPM for petroleum hydrocarbons, the mechanical loading potential of SPM, along with distribution patterns and abundance of SPM, are potentially important parameters of the transportation and fate of spilled oil in Alaskan coastal waters.

Although numerous studies have been performed on the adsorption of oil to SPM (Gearing et al., 1980; Zurcher and Thuer, 1978; Payne, et al., 1984), the detailed dynamics of this process have not been described in a quantitative manner. In general, the variability in bulk oil characteristics such as density and viscosity must be considered, but the key controlling variable appears to be the amount of SPM, and specifically the percent clay in the SPM (Zurcher and Thuer, 1978; Meyers and Quinn, 1973; Payne et al., 1981; Meyers and Oas, 1978; Bassin and Ichiye, 1977). These investigators generally agree that, at equilibrium, between 120 mg and 300 mg of hydrocarbons are incorporated into each kilogram of clay sediment.

Studies of oil spills have shown that in order for significant quantities of oil to reach the bottom, oil must sorb to suspended sediment and sink. The Santa Barbara oil spill is a good example (Kolpack et al., 1971), where transport and deposition of large quantities of flood runoff material occurred during the spill. This appears to be the major transport route of oil to the benthos (Figure 2), although other mechanisms can become significant in certain cases (Figure 3). Most notably, the water column to benthic transport of oil can occur by fecal pellet transport (Boehm, et al., 1982; Johanssen, et al., 1980), by sinking due to Langmiur circulation, or by direct sinking of dense (cold, weathered) oil in areas of low density water (Figure 4) (fresh water input at river mouths or near ice melting). Studies by Juszko, et al., (1983) have suggested that the weathering of oil, typically of an initial density of 0.9 g/ml can create a residue having a density of 1.02 to 1.03 g/ml. Once oil achieves such a density, which is greater than fresh ice melt, oil can sink. The behavior of oil, once it sinks, will be determined by the vertical density structure of the water column. In coastal Alaskan waters, oil may sink to the bottom by this mechanism.

Under conditions of low suspended particle concentrations in the water column (1 to 10 ppm), no significant quantitative transport of particle-sorbed oil to the benthos will occur. Under conditions of moderate suspended particle concentrations (10 to 100 ppm), significant quantities of oil may be sorbed to particles if sufficient mixing of oil and available particles occurs. Under extreme conditions of influx of particles (100 ppm) and mixing of oil and particles in the water column, massive transport of sorbed oil to the offshore benthos can occur with possible severe offshore impact (see Figure 2).

The transport of biologically pelletized oil (zooplankton fecal pellets) to the bottom certainly has occurred and has resulted in analytically detectable oil residues in the bottom with some biological consequences (Johanssen et al., 1980). In some spill scenarios, this may represent the major transport path to the benthos with regards to the overall fate of the mass of spilled oil.

Sedimentation of petroleum hydrocarbon residues directly to the seafloor may occur where discharge of organic-laden drilling fluids occurs. This process depends on the nature of the associated hydrocarbons. A light distillate such as diesel oil or a light fuel oil will largely (80%) partition into the aqueous phase or evaporate (Breteler et al., 1985). Heavier oil and hydrocarbons associated with the formation during drilling are more apt to remain associated with particles and settle with drilling mud particles.

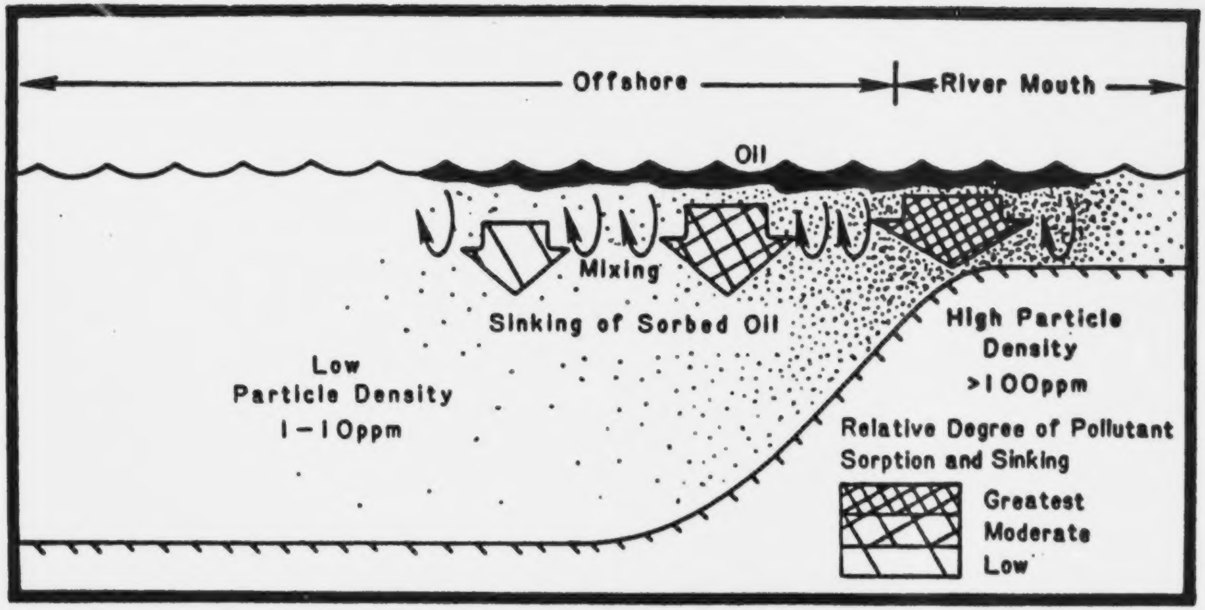

Offshore
River Mouth
Oil
Mixing
Sinking of Sorbed Oil
Low
Particle Density
1−10ppm
High Particle
Density
>100ppm
Relative Degree of Pollutant
Sorption and Sinking
Greatest
Moderate
Low

Figure 2. Transport of oil to benthos due to sorption and sinking.

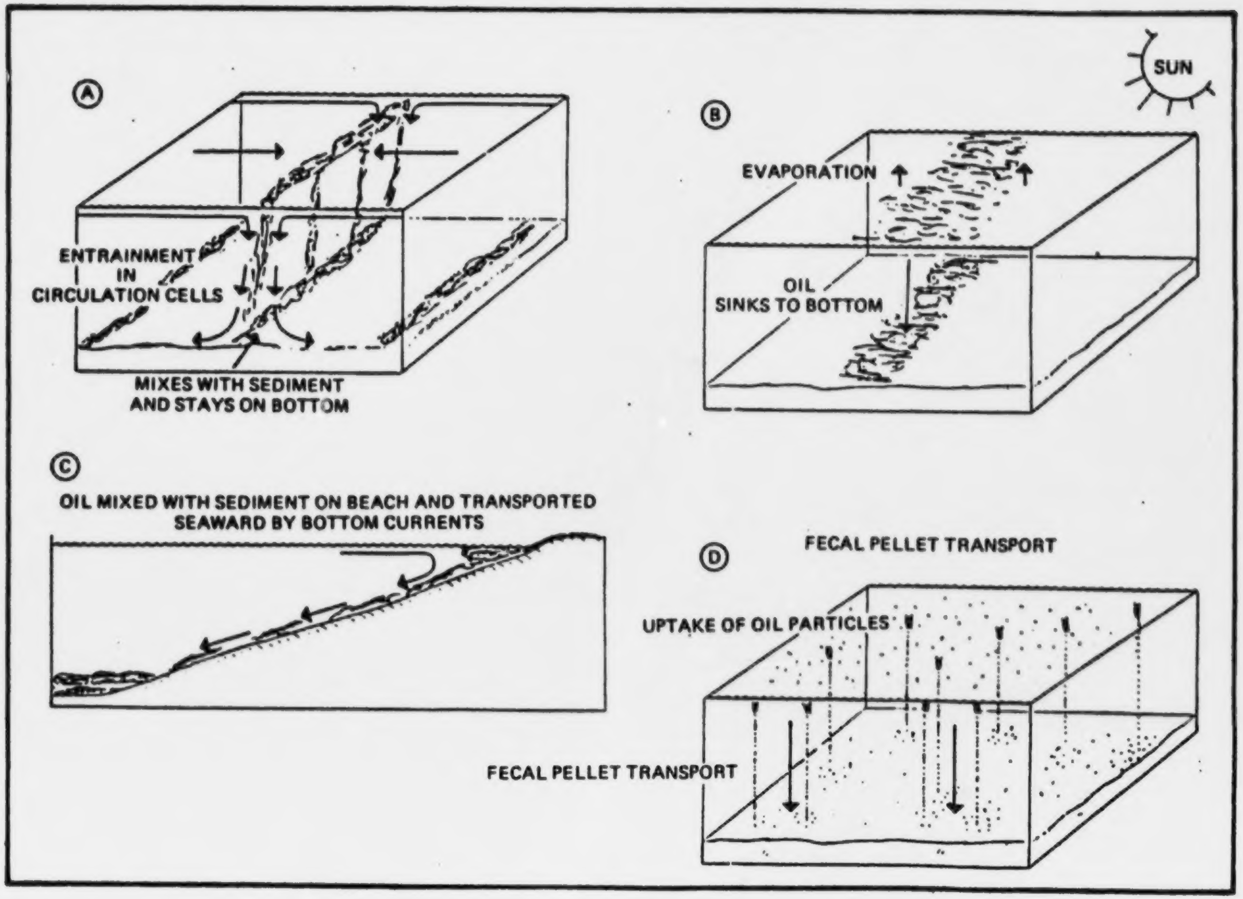

A
ENTRAINMENT IN CIRCULATION CELLS
MIXES WITH SEDIMENT AND STAYS ON BOTTOM
B
SUN
EVAPORATION
OIL SINKS TO BOTTOM
C
OIL MIXED WITH SEDIMENT ON BEACH AND TRANSPORTED SEAWARD BY BOTTOM CURRENTS
D
FECAL PELLET TRANSPORT
UPTAKE OF OIL PARTICLES
FECAL PELLET TRANSPORT

Figure 3. Hypothesized methods by which oil sinks and remains on the bottom.

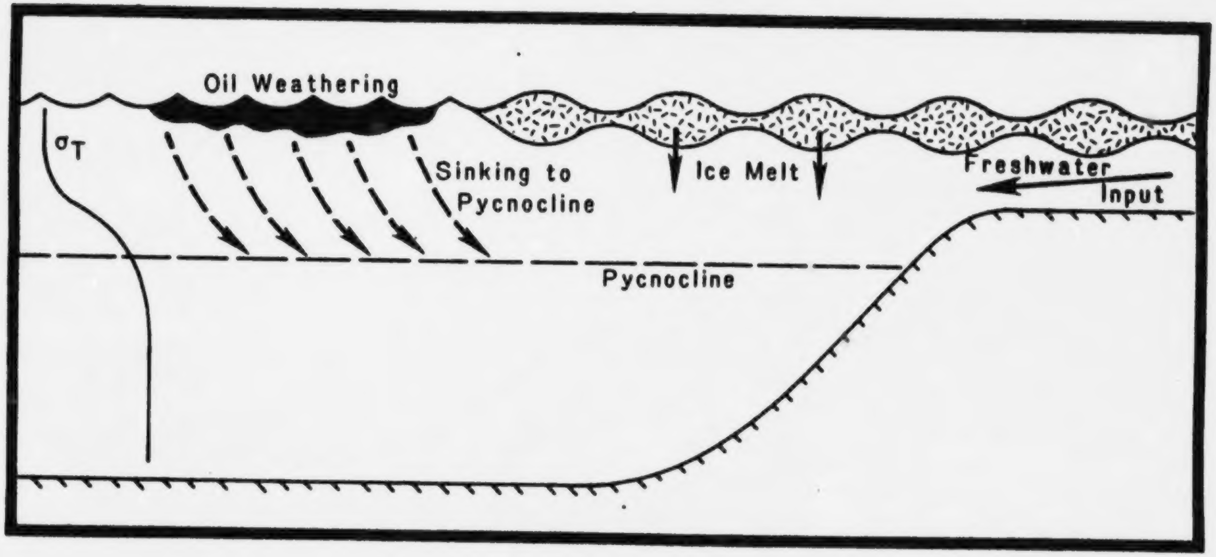

Oil Weathering
σ_T
Sinking to Pycnocline
Ice Melt
Freshwater Input
Pycnocline

Figure 4. Transport of weathered oil to benthos in low-density water.

The amount of petroleum hydrocarbons reaching the sediments by any of the possible transport paths depends on water depth (and hence dilution) and the offshore settling regime (i.e., waves, currents and tidal energy).

It is also widely accepted that significant transport of petroleum components including toxic aromatics to nearshore sediments will occur after beaching of oil, followed by beach erosion and/or ice scour. Studies in the Canadian Arctic (Baffin Island Oil Spill Program, Boehm et al., 1985) and in the Amoco Cadiz spill (Marchand and Caprais, 1981; Boehm et al., 1981; Atlas et al., 1981; Gundlach et al., 1983) have shown that large amounts of oil (100 ppm in sediments) can be expected to impact nearshore (subtidal sediments) if shoreline impact is allowed to occur.

The interaction of oil and sea ice represents a specialized case which is particularly of significance in Alaskan waters. Numerous studies of the physical interactions of crude oil and sea ice have been undertaken (e.g., Lewis, 1976; NORCOR Engineering, 1975). When oil is released into the water column, the oil droplets rise and upon coming in contact with ice, spread under ice and accumulate in depressions. As additional ice freezes under the ice sheet, the oil is effectively trapped. The trapped oil penetrates only slightly into the ice sheet until thawing begins at which point oil penetrates into brine channels within the thawing ice. During this period of time the oil is cut off from evaporation, the mechanism that allows volatile aromatics to "escape" the water column. The effects on under-ice biological communities of exposure to the relatively toxic unweathered oil are likely to be severe. Eventually the trapped oil, which may have been transported over considerable distances while entrapped, escapes to weather normally.

Case Studies

Of particular relevance vis-a-vis the fate of petroleum and petroleum aromatics in Alaskan waters are results from the Amoco Cadiz Oil Spill; the IXTOC I blowout; the Tsesis Oil Spill and the Baffin Island Oil Spill (BIOS) experiments.

The fate of the Amoco Cadiz cargo of crude oil has been extensively studied by Atlas et al. (1981), Boehm et al. (1981), and Gundlach et al. (1983). Gundlach et al. (1983) have conducted perhaps the most rigorous mass balance of spilled oil ever undertaken. Their results are summarized in Figure 5. In this spill, a massive beaching, and other direct introduction of oil into the nearshore sediments and a mixing of oil into the anoxic sediment layers resulted in a long term (3+ years) impact of oil. Biodegradation did not affect oil in the sediment's anoxic zone (Winfrey et al., 1982) and the oil remained toxicologically potent for long periods of time. The most persistent hydrocarbon components, both in the sediments and in benthic animals, were the abundant three ringed PAH compounds (i.e., phenanthrenes) and the polycyclic aromatic sulfur compounds, the dibenzothiophenes, present at 1-10 ppm out of a total aromatic hydrocarbon concentration of 1000 ppm. Most of the 1000 ppm consisted of uncharacterized PAH compounds.

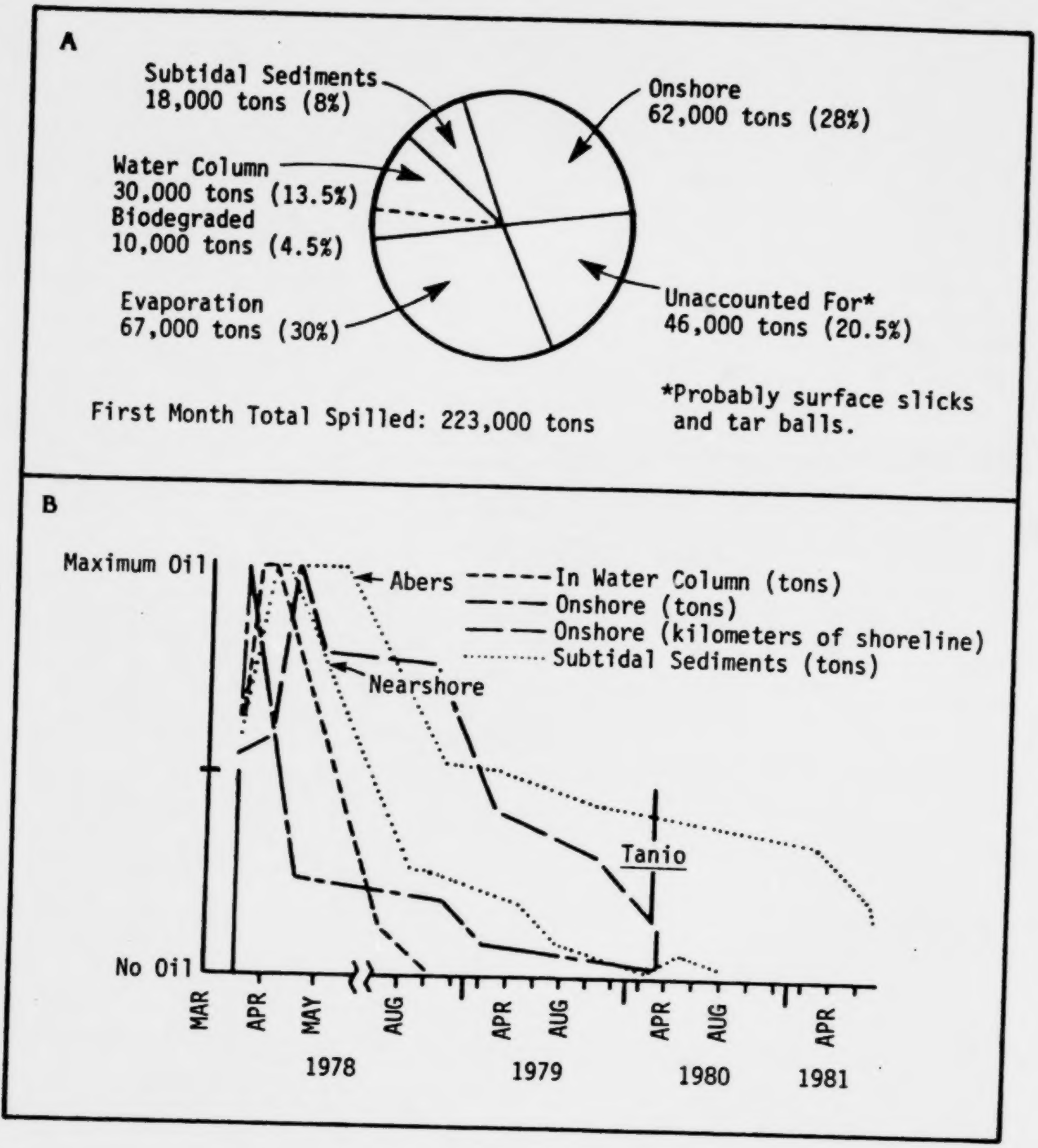
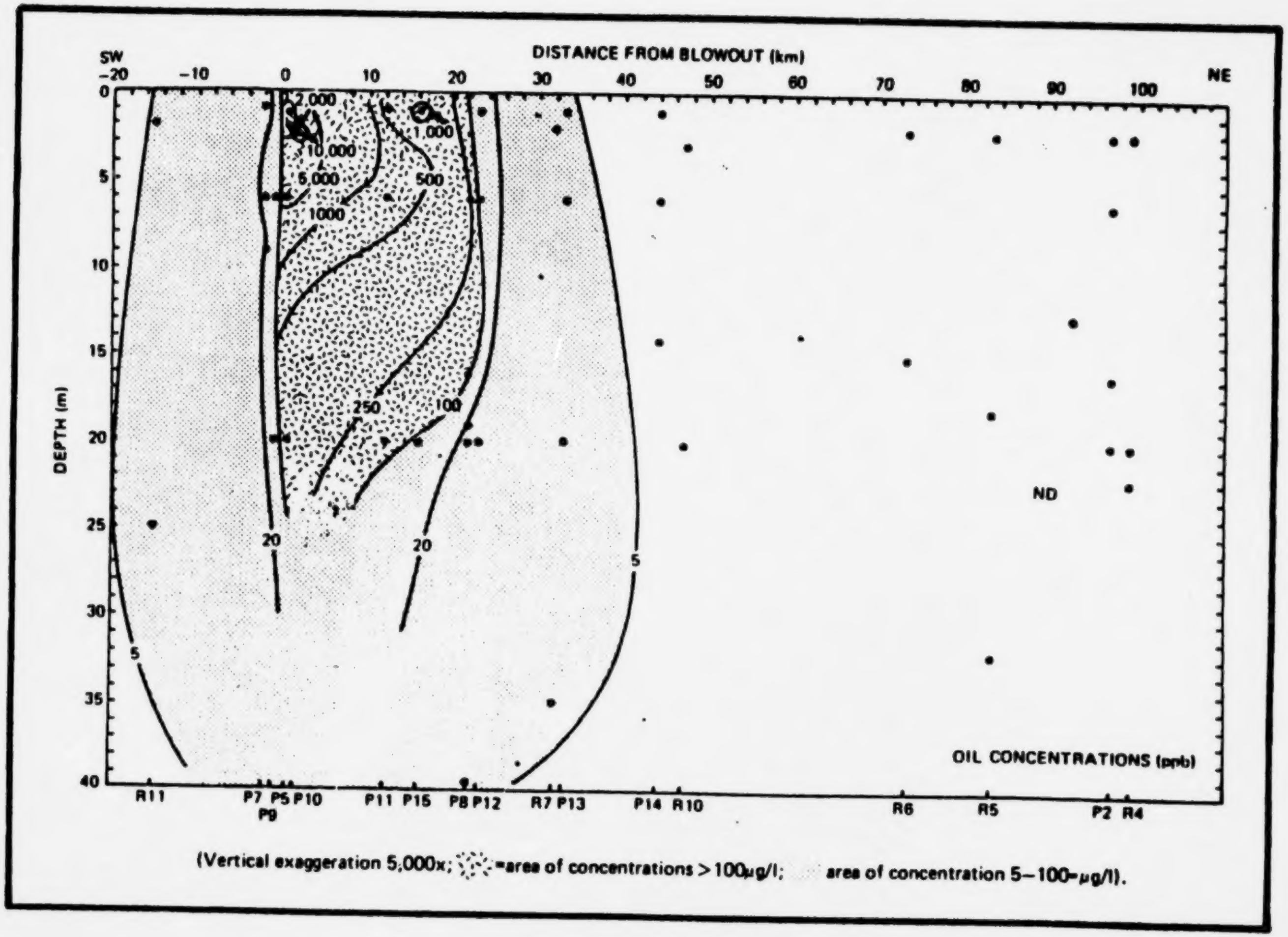


Figure 5. Mass balance results from the Amoco Cadiz oil spill from Gundlach et al., (1983). A - Quantitative estimate of oil fates for the first month after the spill; B - Synthesis of data indicating the relative persistence of oil in various compartments (*Tanio* = a new oil spill event.)

The IXTOC I blowout, in the Gulf of Mexico is hardly typical of an Alaskan spill. However, subsequent studies of the BIOS program have indicated that the results from Boehm and Fiest's (1982) IXTOC I water column studies are quite relevant. These authors found that, due to the undersea nature of the IXTOC blowout, petroleum residues persisted in the water column for up to 40 km from the blowout site. While concentrations dropped off rapidly, an important subsurface plume of oil droplets mixed with an aromatic-enhanced dissolved/colloidal mass was advected up to 20 km from the blowout site (Figure 6). This was a result of a relatively high current speed (0.5-1 knot) and a neutrally bouyant oil mass introduced at the sea floor and rising only slowly to the surface. The ultimate fate of this oil was not determined, but the investigators hypothesized that a significant mass of oil (approximately 30% of the spill) evaporated, with another 30% remaining at the water surface as tar balls, and perhaps another 10-30% of the oil sorbed to particulates and possibly distributed over a wide area in the bottom sediments.

The BIOS program was conceived and executed to examine the comparative fate and effects of crude oil discharged into nearshore Arctic environments and either (1) dispersed chemically or (2) left untreated and allowed to impact the shoreline. The subsurface nature of the discharge of the oil-chemical dispersant mixture allowed for comparison with the IXTOC blowout. It was found that the chemically dispersed plume consisted of neutrally buoyant droplets of relatively unweathered oil similar in composition and behavior to the IXTOC plume, despite drastically different temperature regimes. These plumes persisted for considerable periods of time (hours to several days) in the water column. No significant sedimentation of chemically dispersed oil occurred, nor was there any significant beach impact. By contrast, the untreated oil spillage did result in a massive beaching of the oil. Of the untreated oil initally impacting the beach, 0.2 to 2% was eroded and transported offshore after 1 year. This value increased to 1-10% after two years. Boehm et al., (1985) hypothesized that this erosion would continue to result in increased subtidal oil levels with time. The other main conclusions of this study were (Boehm et al., 1985):

- Chemically dispersing the oil resulted in large initial water column concentrations (50 ppm).
- Initial water-borne oil concentrations under the untreated surface oil slick were low and were confined to the top 1 meter of the water column.
- Longer-term monitoring (one and two years post spill) revealed only low levels of water column oil in all bays (1 ppb or less).
- Subtidal sediment impact was low (10 ug/g) due to chemically dispersed oil-sediment interactions. However, sediment oil concentrations due to the untreated oil increased over two years (up to 400 ug/g) as oil eroded from the beach.



(Vertical exaggeration 5,000x; ⁘ =area of concentrations >100μg/l; ▨ area of concentration 5–100-μg/l).

Figure 6. Concentrations of oil along a transect oriented to the northeast of the IXTOC I blowout, September, 1979.

- Compositional determinations indicated that biodegradation occurred in the beach sediments, but did not occur subtidally.

- The dispersed oil discharge resulted in an initially large bioaccumulation of water-borne oil by all bivalves (up to 700 ppm). Concentrations decreased with time so that two years after the spill most species had returned to near-background levels. Initial tissue levels did not directly reflect water column exposures as animals tended to reduce or cease filtration when exposed to large quantities of petroleum hydrocarbons.

- Initial subtidal benthic faunal impact due to the untreated oil release was low. Concentrations of petroleum hydrocarbons in deposit feeders were, however, seen to increase with time while concentrations in filter feeders decreased.

- Biodegradation of oil occurred within the gut of all benthic animals.

The conclusions of the comparative analyses of the fate of chemically dispersed and untreated oil in the Arctic are summarized in Figure 7. From this analysis, it may be concluded that the net result of the dispersed oil release was a short-term extensive water column and related bioaccumulation impact with little offshore or beach sediment impact. The benthic animals exposed to this dispersed oil depurated steadily, but took approximately 2-3 years or more to return to pre-spill chemical conditions.

In contrast, the water column hydrocarbon impact from the untreated oil release was minimal. However, the stranding of untreated oil on the beach resulted in a long-term source of oil to subtidal sediments and increasing of levels over time of hydrocarbons in benthic animals.

The Tsesis oil spill occurred in the archipelago, south of Stockholm, Sweden in 1977. An extensive interdisciplinary study was undertaken for several years. The results are presented in Kineman et al (1980), Linden et al (1979), and Boehm et al (1982). Several findings regarding the fate of the distillate oil spilled are of particular interest. During the weeks following the spill, many of the zooplankters contained visible oil droplets in their gut. Subsequently, significant quantities of oil were sedimented via the fecal transport route to the bottom. Ten to fifteen percent of the oil spilled during this event was sedimented via incorporation into fecal pellets or adsorption onto suspended sediment particles, as evidenced from sediment trap studies. The monitoring strategy of examining filter-feeding bivalves (*Mytilus edulis*) as indicative of water column oil exposure, and deposit-feeding bivalves (*Macoma balthica*) as indicators of sediment exposure was extremely effective in this study. This strategy was used successfully again in the BIOS program and indicated that inital water column exposure is large, but that complete tissue depuration of aromatic hydrocarbons occurs in one to three years. In contrast, oil residues persist longer in the bottom sediments where chronic exposure persists for many years (more than 3 years), the duration depending on the continued source of hydrocarbons to the benthos.

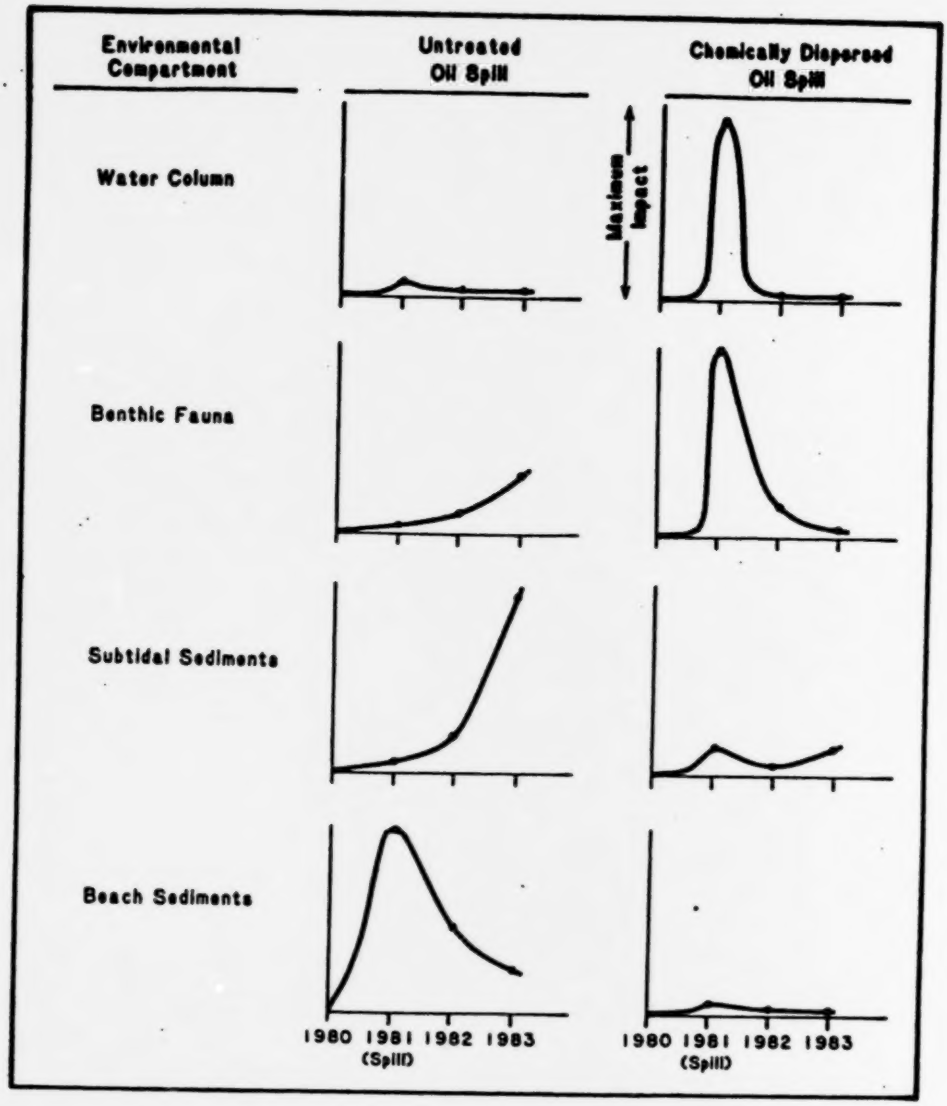


Figure 7. Summary of comparative fates of oil from the BIOS experimental spill.

ALASKAN PERSPECTIVE

Hydrocarbon assemblages in sediments of the Alaskan coastal and offshore areas investigated to date appear to be primarily of natural biogenic origin. Evidence of pyrogenic PAH assemblages presumably derived from deposition of airborne particulate PAH has been reported even in sediments from fairly remote areas. When oil is spilled in arctic and subarctic marine environments similar to those in Alaska, it tends to be more persistent than oil spilled under similar circumstances in temperate and tropical climates. In coastal areas characterized by high suspended sediment loads, such as Cook Inlet, the Beaufort Sea and parts of Norton Sound off the Yukon River, petroleum-derived aromatic hydrocarbons will rapidly adsorb to suspended particles and be transported to the bottom. In bottom sediments, they may be quite persistent. Evaporation of the more toxic low molecular weight aromatic hydrocarbons is impeded by low water temperatures and particularly by ice cover.

4. TRANSFORMATION AND DEGRADATIVE PROCESSES

Aromatic hydrocarbons in the marine environment are subject to chemical transformation and degradation through a variety of processes. The most important of these are photo-oxidation, chemical oxidation and biological transformation by marine bacteria, fungi, plants, and animals. Since a majority of natural mechanisms of oxidative transformation of PAH require molecular oxygen, sunlight, or both, PAH are generally quite stable and persistent once incorporated into oxygen-poor bottom sediments of water bodies.

PHOTODEGRADATION

Zepp and Schlotzhauer (1979) and Mill et al. (1981) have shown that when PAH are present in solution in "pure" fresh or sea water, direct photolysis reactions are quantitatively the most important mechanisms of light-induced transformation of PAH. These direct photochemical transformations can take place in the absence of molecular oxygen. There is a strong tendency for sensitivity to direct photolysis in the aqueous phase to increase with increasing PAH molecular weight (Table 5). Thus naphthalene is quite insensitive to photolysis, while benzo(a)pyrene is quite sensitive. Linear PAH like anthracene and naphthacene are much more sensitive than angular or condensed PAH like phenanthrene and chrysene. Because light intensity decreases rapidly with depth in the water column, rate of PAH photolysis also decreases with depth (Table 5). Sorption to bottom sediments decreases photolysis rate further, particularly of higher molecular weight PAH.

In natural marine and fresh waters, dissolved and particulate substances in the water column may either inhibit or enhance the rate of PAH photochemical transformation (Zadelis and Simmons, 1983; Zepp et al., 1984). Inhibition of photolysis may be due to light attenuation or the direct inhibition of photochemical reactions in various ways.

Other chemicals may serve as sensitizers, increasing the rate of photochemical transformation of other chemicals. Dissolved humic and fulvic substances, algal cells, detritus, and even inorganic particles may increase the rate of photolysis of some PAH under the influence of sunlight, presumably by acting as sensitizers. Humic and fulvic acids from different sources and different species of phytoplankton have similar photosensitizing abilities.

TABLE 5. COMPUTED HALF-LIVES FOR THE DIRECT PHOTOCHEMICAL TRANSFORMATION OF SEVERAL PAH. The time required for one-half the PAH molecules to react near the surface of freshwater (simulated latitude, 40°N, mid-day, mid-summer), at 5 m depth, and at 5 m partitioned to bottom sediment (From Zepp and Schlotzhauer, 1979, with permission of Ann Arbor Science Publishers)

Compound	Half-Life (Hours)		
	Surface	5 Meters	5 Meters (Partitioned)
Naphthalene	71	550	550
1-Methylnaphthalene	22	180	190
2-Methylnaphthalene	54	410	440
Phenanthrene	8.4	59	69
Anthracene	0.75	4.5	4.2
9-Methylanthracene	0.13	0.79	1.2
9,10-Dimethylanthracene	0.35	-	-
Pyrene	0.68	4.2	5.9
Fluoranthene	21.0	160	200
Chrysene	4.4	13	68
Naphthacene	0.034	0.20	0.95
Benzo(a)pyrene	0.54	3.2	13
Benz(a)anthracene	0.59	3.7	9.2

At high latitudes, the rate of photolysis of organic chemicals is greatly diminished due primarily to the reduced intensity and daily duration of solar irradiance during the winter (Figure 8). At 60°N latitude, there is an approximately 10-fold decrease in the rate of photolysis of benzo(a)pyrene between June and December (Zepp and Baughman, 1978). Low temperature in the winter, and certainly ice cover, would reduce the rate of photochemical reactions further.

The situation apparently is quite different in an oil slick on the surface of the water. Here the primary mechanism of photodegradation of PAH is photo-oxygenation involving singlet oxygen (Larson et al., 1976, 1977). Major photoreaction products of PAH are peroxides, phenols, acids, and carbonyls.

There are few direct observations of petroleum photo-oxygenation following major oil spills. Several alkyl-substituted dibenzothiophene sulfoxides were identified in crude oil samples collected from the water near the Amoco Cadiz spill (Calder et al., 1978; Patel et al., 1979).

Overton et al. (1980) layered crude oil from the IXTOC spill on seawater in aquaria exposed to direct sunlight. After 4 days, a number of benzoic acids, substituted naphthenoic acids, phenanthroic, benzothiophenoic and dibenzothiophenoic acids were identified in the extracts. There also was evidence of side-chain oxidation of C1- and C2-substituted naphthalenes.

Recent laboratory and field studies have demonstrated that photo-oxygenation reactions played an important role in the weathering and transformation of Ekofisk crude oil as a surface slick on sea water (Tjessem and Aaberg, 1983; Tjessem et al., 1983). The field studies were conducted along the coast of Norway at 60°N latitude in June, and so resemble conditions that might occur along the southern and western coast of Alaska. However, the Beaufort Sea is at about 70°N and sea temperatures are much lower and ice cover much more prolonged. The high molecular weight resin/asphaltene fraction of the oil reacted rapidly with oxygen. Lower molecular weight aromatics, such as phenanthrene, were converted to polar oxidation products which tended to bind tightly, possibly covalently, to the resin/asphaltene fraction. In related studies, Barth (1984) investigated photo-oxygenation of Ekofisk crude oil in 1-m x 20-m deep plastic bags deployed in the ocean and of Statfjord crude oil discharged at sea at 65°N latitude in August. In the bag experiments, polar hydrocarbon fractions dominated the hydrocarbons in the water column after the second day, and their concentration continued to increase for about two weeks. The composition of this polar fraction was not determined, but had properties similar to those of aliphatic and aromatic alcohols, phenols, and carboxylic acids. Similar polar fractions, presumably consisting of photo-oxygenation products of oil hydrocarbons, were not observed in the water column under the field spill. This was attributed to the much greater dilution of soluble materials in the field and to overcast weather conditions during the spill. The major mechanism of loss of low molecular weight aromatic hydrocarbons (benzenes- naphthalenes) from spilled oil is through evaporation (Riley et al., 1980). However, formation of stable oil-water emulsions, mousses, and pavements tends to slow evaporation of light

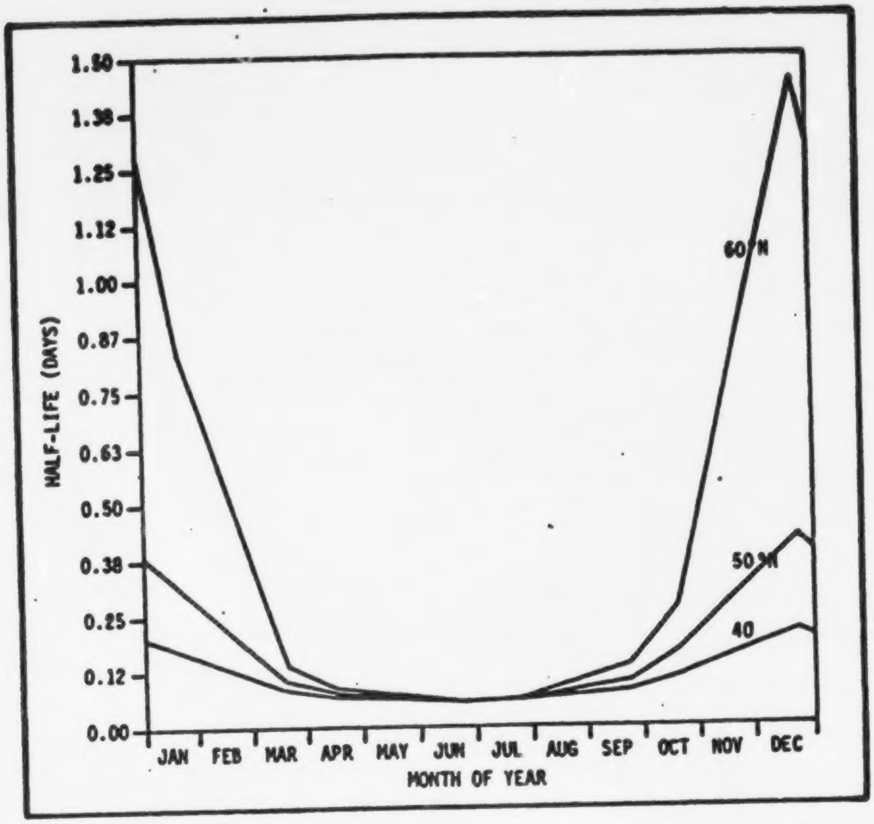


Figure 8. Annual variation of the near-surface half-life (t50) of benzo(a)pyrene at several northern latitudes. (From Zepp and Baughman 1977).

hydrocarbons (Payne et al., 1981a,b; 1983; Boehm and Fiest, 1982). Hardened pavements of spilled oil on or buried in coastal sediments may retain virtually unweathered oil inside a crust of hardened weathered asphalt. Such pavements may persist for years, providing a potential source of fresh oil to the environment, should they be broken up by storms or other disturbances.

TRANSFORMATION BY BACTERIA, FUNGI, AND ALGAE

Bacteria and fungi show tremendous diversity and adaptability in utilization of different organic molecules as a sole carbon source. Some microorganisms are able to oxidize some aromatic hydrocarbons completely to carbon dioxide and water and use them as a source of energy and as a source of carbon for biomass accretion.

Others are not able to carry out this complete oxidation of aromatics, but if an alternative growth substrate is available, they are able to metabolize them partially to various oxygenated metabolites. The latter process is called co-oxidation or co-metabolism (Gibson, 1977). Co-metabolism is thought to reflect a metabolic mistake by the microorganism, due to incomplete enzyme specificity. In addition, certain autotrophic bacteria, fungi, and algae can oxidize aromatic hydrocarbons during photosynthesis, possibly deriving additional energy from the heterotrophic process (Cerniglia, 1981).

An extremely important feature of the bacterial pathway is that the *cis*-dihydrodiol apparently is produced through a dioxetane intermediate, whereas in the mammalian microsomal system, a *trans*-dihydrodiol is produced through an arene oxide intermediate. The arene oxides, or their immediate oxidation products, appear to be responsible for the carcinogenicity or mutagenicity of PAH showing these properties (Oesch, 1982). However, bacteria may be able to metabolize some PAH to mutagenic or carcinogenic metabolites. Microbial methyl hydroxylation of 7,12-dimethylbenz(a)-anthracene to a carcinogenic product has been reported (Wu and Wong, 1981).

In most cases, complete degradation of higher molecular weight PAH to CO_2 and water proceeds very slowly or does not occur. Instead, various phenolic or acidic metabolites are produced (Gibson, 1977).

Fungi (yeasts and molds), unlike bacteria, metabolize PAH by a cytochrome P450- mixed function oxygenase system somewhat similar to that found in mammalian liver microsomes (Cerniglia, 1981). As in the mammalian microsomal system, the initial product of fungal attack on PAH is a *trans*-dihydrodiol produced through an arene oxide intermediate. Many species of fungi from freshwater and marine environments are able to metabolize naphthalene and other PAH, presumably by the arene oxide-trans-dihydrodiol pathway (Cerniglia, 1981). Abundance of fungi was three times higher near (0.2 m) the Cape Simpson, Alaska oil seep than at locations 50 m away (Barsdate, 1973).

Several marine micro- and macro-algal species are able to metabolize naphthalene and to a lesser extent higher molecular weight PAH (Cerniglia, 1981; Kirso et al., 1983; Van Baalen and Gibson, 1984). In some cases, the primary metabolic products of BaP degradation in the presence of algae are quinones, suggesting that the algal cells are serving as sensitizers for photo-oxygenation of the PAH. In addition, phenol oxidases, which are present in high concentration in some algae, could mediate the non-specific enzymatic oxidation of PAH to quinones. None of the diatoms from Cook Inlet or from the ice edge in the Bering Sea, examined by Van Baalen and Gibson (1982), could metabolize naphthalene completely to CO_2. However, they could metabolize it to 1-naphthol. The investigators suggested that in cold marine environments, the rate of aromatic hydrocarbon metabolism by marine phytoplankton might be a significant fraction of the rate of aromatic hydrocarbon metabolism by marine bacteria.

Many studies have been performed on ability of marine water column and sediment bacteria to degrade petroleum hydrocarbons, including PAH. Aliphatic and aromatic hydrocarbons are degraded much more rapidly under aerobic than anaerobic conditions (Lee et al., 1978; Ward et al., 1980). Rate of PAH degradation tends to decrease with increasing PAH molecular weight (Readman et al., 1982). Bacterial populations from oil-contaminated areas metabolize PAH more readily than populations from clean areas (Saltzman, 1982).

Lee and Ryan (1983) reported that naphthalene and phenanthrene were fairly rapidly biodegraded in water samples from the Rhode Island and Georgia-South Carolina coasts. Medium molecular weight PAH (anthracene, fluorene, benz(a)anthracene and chrysene) were not readily biodegraded in the water column, but were degraded rapidly in sediment-water slurries. Higher molecular weight PAH (dimethyl-benz(a)anthracene, dibenz(a,h)-anthracene, and benzo(a)pyrene) were not readily biodegraded even in sediment-water slurries. When PAH were added to water or sediment samples from areas with little or no hydrocarbon pollution, there was a lag period of at least one day before significant degradation occurred. The rate of degradation of PAH was much more rapid in sediments from oil-contaminated areas and there was no lag before initiation of degradation. Benz(a)anthracene added to a sediment-water slurry from oil-contaminated Shipyard Creek, South Carolina, in August (29°C) was degraded at a rate of about 95 ng/g sediment/day, whereas the rate of degradation was about 14 ng/g sediment/day in a clean sediment-water slurry from the nearby Skidway River, Georgia, at a temperature of 28°C.

Temperature had a profound effect on the rate of degradation of PAH in water or sediments (Lee and Ryan, 1983). For example, the calculated half-life for degradation of phenanthrene at an initial concentration of 25 ug/liter in sea water was 79 days in June at a temperature of 18°C and 11,000 d in January at a temperature of 2°C. The half-life of benz(a)anthracene at a concentration of 2.5 mg/kg in sediment increased from 1,100 days in October at 15°C to 21,000 days in February at 4°C. The authors also showed that dimethylbenz(a)anthracene in water was degraded slowly by a combination of photochemical and microbial processes.

Photo-oxygenation reactions produced mono-hydroxy derivitives and quinones, which then were degraded further to CO_2 by resident bacteria.

Following a spill of crude or refined petroleum, different hydrocarbon components and classes are degraded simultaneously, but at widely different rates by indigenous water column and surficial sediment microbiota (Bartha and Atlas, 1985). Low molecular weight n-alkanes in the C10-C22 molecular weight range are metabolized most rapidly, followed by iso-alkanes, olefins (if present), mono-aromatics, PAH, and finally highly condensed cycloalkanes, resins, and asphaltenes. The result is that microbial degradation, plus evaporation and photo-oxygenation/photolysis markedly change the composition of the oil over time.

The rate of microbial degradation of petroleum hydrocarbons in the water column and in bottom sediments is dependent on many factors, including oxygen and primary nutrients (especially nitrogen and phosphorus) concentrations, temperature, chemical composition of oil, and previous history of hydrocarbon inputs to the area (Atlas, 1981; Bartha and Atlas, 1985). Several attempts have been made to estimate these rates in the field. Butler et al. (1976) quote degradation rates of 1-10 mg hydrocarbons/m^3/day for open-ocean waters. Following the Amoco Cadiz oil spill, in which 190,000 metric tons of crude oil was released to the coastal waters of Brittany, France, Aminot (1981) estimated the rate of microbial degradation of hydrocarbons in the water column under surface oil slicks to be about 30 mg/m^3/day. The rate of microbial degradation of dissolved and microparticulate oil in the water column following the IXTOC 1 oil spill in the Bay of Campeche, Gulf of Mexico, was in the range of 0.24 to 1,056 mg aliphatic hydrocarbon respired/m^3/d (Buckley and Pfaender, 1980; Pfaender et al., 1980).

Rates of degradation of crude and refined oils in oxidized surficial sediments are in the range of 0.02 to 0.40 grams/m^2/day, with an average of 0.14 grams/m^2/day (GESAMP, 1977). Atlas and Bronner (1981) estimated that petroleum hydrocarbons were being degraded in the upper 5 cm of intertidal sediments along the Brittany Coast of France impacted by the Amoco Cadiz oil spill at a rate of 0.05 grams/m^2/day. Extrapolating to the 320 km of coastline impacted by the spill, they estimated that it would take more than 20 years to biodegrade the estimated 64,000 metric tons of oil believed to have impacted the Brittany Coast.

In arctic marine environments, biodegradation of petroleum hydrocarbons appears to proceed quite slowly, possibly due in part to nutrient limitation (Bergstein and Vestal, 1978), low numbers of hydrocarbon-degrading bacteria (Atlas et al., 1981; Atlas, 1984), and low temperatures (Cundell and Traxler, 1973; Gibbs et al., 1975). Atlas et al. (1978) simulated spills of Prudhoe Bay crude oil on water during summer near Point Barrow, Alaska. There was a 22 percent loss of oil during the first month, due primarily to evaporation and/or dissolution of low molecular weight hydrocarbons. An additional 3 percent was lost during the second month and was attributed primarily to microbial activity. During winter, crude oil spilled on the ice lost only 5 percent of its weight in nine months, due primarily to evaporation, with no indication of any biodegradation. Oil spilled under ice showed a small transport of hydrocarbons during three weeks, due to dissolution. Oil-contaminated sediments placed in 5 meters of water lost 45 percent of hydrocarbons in 60 days during May and June. These losses were attributed primarily to biodegradation.

In subsequent experiments performed in Elson Lagoon near Point Barrow, Haines and Atlas (1982) followed degradation of hydrocarbons over a two-year period. Total microbial biomass remained relatively constant in the oil-contaminated sediments. After 1 to 4 months, numbers of hydrocarbon-utilizing bacteria increased slowly, but their numbers never exceeded 4×10^{-3} percent of the total microbial biomass in the surficial sediments. Microbial degradation of the sediment hydrocarbons, as indicated by a decrease in the n-alkane/isoprenoid hydrocarbon ratio, became evident only after 1.5 years of exposure. Concentrations of aromatic hydrocarbons in the naphthalene, phenanthrene, and dibenzothiophene series in sediments decreased very slowly. The authors concluded that microbial degradation of petroleum hydrocarbons in arctic marine environments of Alaska will proceed very slowly. There also was little evidence of microbial degradation of petroleum hydrocarbons in subtidal sediments at the site of the Baffin Island Experimental Oil Spill (BIOS) (Boehm, 1983). It should be kept in mind that the estimates quoted above for the rate of biodegradation of petroleum hydrocarbons in the water column and in bottom sediments are for total hydrocarbons. Since PAH, especially those above phenanthrene, are among the more refractory components of petroleum, their rates of biodegradation will be much lower than those for whole petroleum.

Atlas (1982) examined the species composition of water column and sediment bacteria from coastal and outer continental shelf waters of all coasts of Alaska. He reported that hydrocarbon-degrading bacteria were indigenous to all Alaskan coastal waters and sediments. However, they were present in low numbers, particularly in the water column. Atlas concluded that the oil-degrading ability of these bacterial populations is not sufficient to extensively degrade spilt oil before it impacts sediments and coastlines. He suggested that the rate of petroleum hdyrocarbon degradation in Alaskan OCS regions would be slow, and hydrocarbon pollutants resulting from accidents during OCS oil development and production would persist for long periods.

TRANSFORMATION BY MARINE ANIMALS

In most invertebrate and vertebrate animals studied to date, an enzyme system variously known as the cytochrome P450-dependent mixed function oxidase, mixed function oxygenase (MFO), aryl hydrocarbon hydroxylase, or drug metabolizing system is responsible for initiating the metabolism of various lipophilic organic compounds, including xenobiotics (foreign organic compounds such as alkenes, PAH, pesticides, and drugs) and endogenous compounds such as steroid hormones and bile salts.

The primary function of this system appears to be to render poorly water-soluble lipophilic materials more water-soluble and therefore more available for excretion. Although this system effectively detoxifies certain xenobiotics, others, such as certain PAH and alkenes, may be transformed to intermediates which are highly toxic, mutagenic, or carcinogenic to the host. Oxidative metabolism of PAH in this system proceeds via highly electrophilic intermediate arene oxides, some of which bind covalently to cellular macromolecules such as DNA, RNA, and protein. It is now generally agreed that metabolic activation by the mixed function oxygenase (MFO) system is a necessary prerequisite for PAH-induced carcinogenesis and mutagenesis (Oesch, 1982).

The MFO system is located in the liver and usually also in several other organs of many invertebrates and vertebrates. Within the cell, it is localized primarily in association with the smooth endoplasmic reticulum (smooth microsomal fraction) (Stasiecki et al., 1980).

Considerable progress has been made in identifying and quantifying the MFO system and its components in marine invertebrates and vertebrates (See reviews of Neff, 1979, 1984; Lee, 1981; Stegeman, 1981). Among the invertebrates, mixed function oxygenase activity seems to be highest in some members of the phyla Arthropoda and Annelida. Of course, many invertebrate phyla have not been investigated. Coelenterates and ctenophores apparently lack MFO activity. Among the Echinodermata, sea urchins Strongylocentrotus sp. and starfish Asterias sp. have low levels of MFO.

Five species of marine polychaete worms have been examined and all but one species (Arenicola sp.) have at least a limited ability to transform PAH. The situation among the mollusca is more complicated. Several investigators have been unable to detect MFO activity in several species of bivalve molluscs including Mytilus edulis, Mya arenaria, Ostrea edulis, and Anodonta sp. However, Anderson (1978) measured a low level of MFO activity in oysters Crassostrea virginica which have been exposed to BaP for long periods of time. Stegeman (1981) detected traces of authentic MFO activity (BaP hydroxylation) in the marine mussels Mytilus edulis and Modiolus modiolus. Low levels of MFO activity have been reported in snails Littorina sp. and squid Illex illecebrosus (Payne and May, 1979).

Mixed function oxygenase activity has been detected in more than 18 species of marine crustaceans (Neff, 1979; Lee, 1981). Levels of in vitro MFO activity in crustacean hepatopancreatic preparations usually are low and variable. In addition, non-hepatic tissues of crustaceans such as green gland, gonads and stomach may have as high or higher MFO activity than the hepatopancreas. Metabolite identification experiments with several marine crustaceans have shown that the intact animal can produce PAH metabolites very rapidly.

The mixed function oxygenase system has been detected in more than eight species of elasmobranch fish and more than four dozen species of teleost fish. Hepatic microsomal mixed function oxygenase activity varies widely among different species and even among individuals of the same species. These variations do not seem to be related to habitat preference or feeding habits of the fish. There is little difference in the range of MFO activity between freshwater and marine species, or between cold water and warm water species.

In most cases, the types of PAH metabolites produced by marine invertebrates and fish are similar to those produced by mammals. They include PAH dihydrodiols, phenols, and quinones as well as PAH conjugates with sulfate, glucuronic acid, and glutathione. Several species of fish including starry flounder *Platychthys stellatus*, English sole *Parophrys vetulus*, deep-sea rattail fish *Coryphaenoides armatus*, and coho salmon *Oncorhynchus kisutch* liver microsomes metabolize benzo(a)pyrene to a suite of metabolites similar to those produced by rat liver microsomes (Varanasi and Gmur, 1980; Stegeman, 1981; Gmur and Varanasi, 1982; Stegeman, 1983). The major identified metabolites produced by the fish microsomes are the 7,8- and 9,10-dihydrodiols which are precursors of the major carcinogenic BaP metabolite. In fish, as in mammals, most MFO activity is localized in the liver. Gills, kidney, and testes also contain significant MFO activity. Activity in other tissues is low (less than 10% the activity in liver microsomes). Different fish species may have markedly different basal levels of MFO activity.

The pattern among marine invertebrates is quite different. In the blue crab *Callinectes sapidus* and shore crab *Carcinus maenas*, highest BaP hydroxylase activity occurs in the green gland or antennary gland (analogous to the teleost kidney) and the pyloric stomach (Singer and Lee, 1977; O'Hara et al., 1982). The hepatopancreas (roughly analogous to the teleost liver) has low activity. Other crab tissues containing significant MFO activity include gills, testes, eyestalks, nerve ganglia, and heart.

Seasonal changes have been reported in MFO activity in tissues of several species of fish and invertebrates (Bend et al., 1978; Walton et al., 1983). Sexual differences in levels and activities of MFO components have been observed in fish and crustaceans. BaP hydroxylase activity was nearly two orders of magnitude higher in green gland of mature female blue crabs *Callinectes sapidus* than in green gland of mature males of the same species (Singer and Lee, 1977).

Malins et al. (1982) determined the activity of the mixed function oxygenase system in liver or viscera of six species of marine fish and two species of marine invertebrates. All species were indigenous to Alaskan coastal waters. Lowest activity in fish liver was in arrowtooth flounder (*Atharestes stomias*), and highest activity was in Pacific cod (*Gadus mactocephalus*). Activity in tanner crab (*Chionoecetes* sp.) was similar to that in fish liver, while no activity could be detected in snail (*Fusitriton* sp.) tissues. Mixed function oxygenase activity in these Alaskan species was similar to that in similar species from lower latitudes.

Enzyme induction is the process whereby concentration or activity of an enzyme is increased in response to exposure of the organism to the normal substrate of the enzyme. Several investigators have shown that exposure to PAH or complex mixtures of hydrocarbons, such as petroleum, results in rapid (within 1-10 days) induction of elevated levels of MFO activity in some marine fish (See reviews of Lee, 1981; Stegeman, 1981). Different components of the PAH-metabolizing system are induced to different degrees by inducers. Therefore, it is not surprising that the relative proportion of different types of PAH metabolites produced by uninduced and induced hepatic microsomes are different.

Much less research has been performed on induction of MFO activity in marine invertebrates. Several attempts to induce MFO activity in several species of algae, molluscs, crustaceans, annelids, and echinoderms by exposure to PAH or oil have failed. However, Anderson (1978) apparently was able to induce a very low level of BaP hydroxylase activity in oysters *Crassostrea virginica* following exposure for 5-9 months to 1 ug/l benzo(a)pyrene or methylcholanthrene in the ambient medium. Lee et al. (1979) induced MFO activity in the polychaete worm *Capitella capitata* by exposing the worm to benz(a)anthracene or crude oil in its sand substrate for three to ten weeks. Lee et al. (1981) demonstrated induction of MFO activity in sand worms *Nereis virens* by exposure to benzo(a)pyrene or PCBs in the laboratory or oil-contaminated sediments in the field. Exposure of copepods *Calanus helgolandicus* for 7 d to seawater solutions of naphthalene, 2-methylnaphthalene, 3-methylcholanthrene, or benzo(a)pyrene (50-200 ug/l) resulted in significant elevation of BaP hydroxylase activity in whole animal homogenates (Walters et al., 1979).

Salmonids have a well-developed readily inducible hepatic mixed function oxygenase system. Gruger et al. (1977a) reported that mixed function oxygenase was induced in female coho salmon (*Oncorhynchus kisutch*) by exposure for six days to the water-soluble fraction of oil at concentrations as low as 15 ppb. Males were less sensitive. Subsequently, Gruger et al. (1977b) fed saltwater-adapted coho salmon (*O. kisutch*) and chinook salmon (*O. tshawytscha*) test diets containing polychlorinated biphenyls, petroleum hydrocarbons, or both. There was substantial induction of mixed function oxygenase in liver microsomes of coho, but not chinook salmon.

Several investigators have demonstrated induction of MFO activity in fish as a result of exposure in the field to petroleum. Payne (1976) reported significantly higher levels of MFO activity among cunners *Tautogolabrus adspersus* from oil-polluted stations than from unpolluted stations along the coast of the Avalon Peninsula, Newfoundland, Canada. Based on these and other results, he recommended use of fish hepatic microsomal MFO activity as a monitor for oil pollution.

Davies et al. (1981) reported elevated levels of MFO activity in hepatic microsomes of several species of fish from the vicinity of offshore oil production platforms in the North Sea. Spies et al. (1982) studied activity of MFO enzymes in two species of flounder, *Citharichthys sordidus* and *C. stigmaeus* from coastal southern California. Highest hepatic MFO activity was observed in flatfish from the vicinity of the Los Angeles County sewage outfall off Palos Verdes, intermediate near the 7-mile Hyperion sewage outfall in Santa Monica Bay and near an oil seep in the Santa Barbara Channel, and lowest in unpolluted waters of Monterey Bay. Payne et al. (1984) reported elevated MFO activity in kidney microsomes of winter flounder *Pseudopleuronectes americanus* from the vicinity of an oil spill in the Baie Verte, Newfoundland.

It is apparent that a great many endogenous and exogenous factors can influence levels of MFO and related enzyme activity and concentrations of MFO components in the tissues of aquatic animals. Each species seems to respond somewhat differently to these factors and there are even significant intraspecific (probably genetic) differences. Endogenous factors may include age, sex, reproductive status, nutritional status, period of the molt cycle (in arthropods), etc. Primary exogenous factors influencing rate of PAH metabolism include temperature, season, possibly salinity (though this has not been studied), and current and previous history of exposure to potential inducers or inhibitors of different components of the microsomal PAH-metabolizing system.

Although induced hepatic MFO activity is a useful and fairly specific index of previous exposure to certain organic pollutants, its utility for assessing environmental damage is limited by lack of a complete understanding of the long-term biological consequences to the fish of elevated MFO activity. MFO induction is a normal adaptive response of the animal and is not by itself an indication of existing or impending pathology. Chronic induction may afford a degree of protection from the inducing pollutant. Alternatively, it may produce pathological side effects by exceeding the capacity of the conjugation system, by altering metabolism of endogenous substrates such as steroid hormones, or by increasing the production of mutagenic and carcinogenic metabolites.

INTERACTION OF DE[illegible]DATIVE PROCESSES IN THE REMOVAL OF PAH FROM THE MARINE ENVIRONMENT

In the marine environment, the assorted oxidative processes that are responsible for degrading PAH do not proceed independently of one another. The nature and extent of interactions between different processes are often hard to ascertain. Lee et al. (1978) introduced dispersed Prudhoe Bay crude oil enriched with a number of PAH into a marine controlled ecosystem enclosure (ca. 2-m diameter and 15-m deep) on the coast of British Columbia, Canada, and estimated rate of loss of different PAH by evaporation, photochemical oxidation, microbial degradation, and sedimentation. Concentrations of added PAH decreased by 50 percent in 3 to 4 days at a depth of three meters and in 4 to 6 days at seven meters. By Day 17, all PAH were below the limit of detection at seven meters. Photolysis appeared to be the main mechanism of BaP degradation in the upper 5 meters. Quinones and more polar materials were the major products of BaP photodegradation. Nearly 40 percent of the BaP introduced into the enclosure was recovered from bottom sediments. BaP and benz(a)anthracene were not metabolized significantly by water-column bacteria. However, naphthalene, methylnaphthalenes and anthracene were metabolized to a small extent by water column bacteria. Naphthalene and methylnaphthalenes, and to a much lesser extent anthracene and fluoranthene, were also lost from the water column by volatilization. A significant fraction of all added PAH sedimented to the bottom of the enclosure adsorbed to colloidal or detrital material. Accumulation and metabolism of PAH by water column organisms, mainly phytoplankton and copepods, contributed little to the degradation of PAH in the system.

This study illustrates the brief residence time of PAH in temperate marine waters. Lower molecular weight aromatics (benzene-phenanthrene) are removed primarily by evaporation and microbial activity. Higher molecular weight PAH are removed mainly by sedimentation and photochemical transformation. Degradation by water column animals is of minor importance. However, as Lee et al. (1979) showed, benthic animals may contribute significantly to PAH degradation by sediment bioturbation. This keeps sediments aerobic so that aerobic sediment bacteria can metabolize the PAH. Hinga et al. (1980) showed in another microcosm study that most of the microbial degradation of PAH (in this case, benz(a)anthracene) takes place in the upper 1-2 cm of sediment (the oxidized layer) and not in the water column or deeper sediment layers. Once buried in anoxic sediments, PAH appear to be extremely persistent.

ALASKAN PERSPECTIVE

The mechanisms of degradation and loss of polycyclic aromatic hydrocarbons from Alaskan marine waters and sediments are the same as those occurring in marine waters and sediments of more temperate and tropical climates. These processes include evaporation, photochemical and chemical degradation, and metabolism by marine bacteria, fungi, phytoplankton, and animals. In Alaskan waters, most of these processes proceed slowly because of low ambient temperatures and low net incident solar radiation during much of the year. In particular, the most important mechanisms quantitatively of PAH removal (i.e., evaporation, photodegradation, and microbial metabolism) appear to proceed very slowly in arctic and subarctic marine waters. Thus, PAH introduced into Alaskan waters by natural mechanisms, intentional discharges or accidental spills will tend to persist and may accumulate over time to high concentrations in Alaskan marine sediments.

5. ACCUMULATION AND RELEASE BY MARINE ANIMALS

It is important to critically evaluate the published literature on the rates of accumulation and release of petroleum-derived aromatic hydrocarbons by marine organisms. The accumulation and release rates are important factors in the prediction or assessment of the long-term impacts of oil spills and chronic discharges on the marine environment and, in particular, on commercial fisheries resources in the spill or discharge area.

BIOACCUMULATION FROM WATER AND SEDIMENT

There is an extensive body of published literature dealing with the bioaccumulation of petroleum hydrocarbons, including low to medium molecular weight aromatics, by marine animals during exposure for different lengths of time to petroleum hydrocarbons accommodated or dispersed in the water column. There have been fewer published reports of bioaccumulation of petroleum hydrocarbons from oil-contaminated sediments. The hydrocarbons most frequently quantified in exposure media and animal tissues were naphthalenes and phenanthrenes.

Table 6 summarizes results of several laboratory studies of bioaccumulation of aromatic hydrocarbons by marine bivalve molluscs, crustaceans, polychaetes, and fish, many of them indigenous to Alaskan coastal waters. Although bioconcentration factors (concentration in tissues divided by concentration in exposure medium) cover a wide range, some general trends emerge. For the few species for which comparative data are available, bioaccumulation factors for aromatic hydrocarbons from sediments are much lower than those from water. Bioaccumulation factors tend to increase with increasing molecular weight, and thus decreasing aqueous solubility, of polycyclic aromatic hydrocarbons.

Bivalve molluscs, which typically demonstrate the highest bioconcentration factors of the taxa studied, may achieve bioconcentration factors of 100 to 36,000. The higher bioconcentration factors usually are associated with long-term exposures to low concentrations of hydrocarbons in water. When bivalves were exposed to relatively high concentrations of petroleum hydrocarbons in sediments, the bioconcentration factors for specific aromatic hydrocarbons were quite low (0.1-10). Roesijadi et al. (1978) showed in a carefully designed laboratory study, that bioconcentration factors in the clam *Macoma inquinata* for four PAH were 0.2 or less from sediment and 10 to 1,349 from the overlying water column.

TABLE 6. SUMMARY OF AROMATIC HYDROCARBON UPTAKE BY MARINE ORGANISMS

		Exposure Conditions			Tissue		
Taxon	Species	Oil/Hydrocarbon	Max. Conc. (ppm)	Time (days)	Concentration (ppm)	Conc. Factor	Reference
		Water					
Bivalves	*Macoma balthica*	Prudhoe Bay Crude (PBC) (total aromatics) (OWD)	0.001	120	15.7	15,700	Clement et al. 1980
	Macoma inquinata	Prudhoe Bay					
		Phenanthrene	0.004	7	0.04	10	Roesijadi et al. 1978
		Chrysene	0.0004	7	0.30	694	
		Dimethylbenz(a)-anthracene	0.0006	7	0.86	1349	
		Benzo(a)pyrene	0.0004	7	0.04	861	
	Mytilus edulis	North Sea crude oil	0.030	140	152.0	5,000	Widdows et al. 1982
			0.036	28	78.0	2,200	
	Rangia cuneata	Produced water (total naphthalenes)	1.7	100	16.0	9.4	Fucik et al. 1977
	Rangia cuneata	Naphthalene	0.071	1	0.43	6.1	Neff et al. 1976b
		Phananthrene	0.089	1	2.85	32.0	
		Chrysene	0.066	1	0.54	8.2	
		Benzo(a)Pyrene	0.052	1	0.45	8.7	
		Total naphthalenes	3.4	1	60.0	17.6	Anderson & Neff 1975
	Rangia cuneata	Benzo(a)pyrene	0.030	1	7.2	240	Neff & Anderson 1975
			0.030	1	5.7	190	
	Rangia cuneata	Naphthalene	0.84	1	1.9	2.3	Neff et al. 1976b
		Methylnaphthalenes	0.4	1	3.5	8.7	
		Dimethylnaphthalenes	0.24	1	4.1	17.1	
		Trimethylnaphthalenes	0.03	1	0.8	26.7	

TABLE 6. SUMMARY OF AROMATIC HYDROCARBON UPTAKE BY MARINE ORGANISMS (CONTINUED)

		Exposure Conditions			Tissue		
Taxon	Species	Oil/Hydrocarbon	Max. Conc. (ppm)	Time (days)	Concentration (ppm)	Conc. Factor	Reference
		Water (con't.)					
Bivalves	*Crassostrea virginica*	Naphthalene	0.005	2	30.0	6,000	Lee et al. 1978
			0.003	8	12.0	4,000	
		Methylnaphthalenes	0.008	2	56.0	7,000	
			0.003	8	36.0	12,000	
		Dimethylnaphthalenes	0.010	2	84.0	8,400	
			0.002	8	72.0	36,000	
	Crassostrea virginica	Anthracene	0.013	2	5.6	431	
			0.001	8	2.5	2,500	
		Fluoranthene	0.007	2	5.0	714	
			0.004	8	4.0	10,000	
		Benzo(a)thracene	0.005	2	2.8	560	
			0.0001	8	1.8	18,000	
		Benzo(a)pyrene	0.002	2	0.36	180	
			0.0001	8	0.30	3,000	
	Crassostrea virginica	Total hydrocarbons	0.106	50	330	3,100	Stegeman & Teal 1973
		Sediment					
Bivalves	*Macoma inquinata*	Prudhoe Bay	6.0	54	2.0	0.3	Augenfeld et al. 1980
		(Total aromatics)	6.0	55	5.2	0.9	Roesijadi & Anderson 1979
	Macoma inquinata	PBC					
		Phenanthrene	2.1-.006	59	0.018	3-6	Augenfeld et al. 1982
		Chrysene	3.3-.01	58	1.3	1-11	
		Benzo(a)pyrene	0.6-.03	60	.15	1-5	

TABLE 6. SUMMARY OF AROMATIC HYDROCARBON UPTAKE BY MARINE ORGANISMS (CONTINUED)

		Exposure Conditions			Tissue		
Taxon	Species	Oil/Hydrocarbon	Max. Conc. (ppm)	Time (days)	Concentration (ppm)	Conc. Factor	Reference
		Sediment (con't.)					
Bivalves	*Macoma inquinata*	Phenanthrene	0.49	7	.10	.20	Roesijadi et al. 1978
		Chrysene	8.37	7	.31	.04	
		Dimethylbenz(a)-anthracene	4.63	7	.30	.06	
		Benzo(a)pyrene	0.64	7	.06	.09	
	Macoma inquinata	PBC (total aromatics)	40	30	5.0	0.13	Anderson et al. 1983
	Macoma inquinata	PBC + dispersant (total aromatics)	40	30	5.0	0.13	Anderson et al. 1985
	Protothaca staminea	Prudhoe Bay (total aromatics)	22	365	0.6	0.03	
	Protothaca staminea	PBC + dispersant (total aromatics)	40	30	1.9	0.05	Anderson et al. 1985
		Water					
Crustaceans	*Penaeus aztecus*	No. 2 fuel oil, WSF (total naphthalenes)	1.9	1	4.0	2.1	Anderson et al. 1974b
			0.3	1	digestive gland 70	233	Neff et al. 1976b
	Penaeus aztecus	No. 2 fuel oil (total naphthalenes)	0.7	1	3	4.3	Anderson 1975
	Penaeus aztecus	No. 2 fuel oil, WSF (total naphthalenes)	0.4	0.5	7	18	

TABLE 6. SUMMARY OF AROMATIC HYDROCARBON UPTAKE BY MARINE ORGANISMS (CONTINUED)

		Exposure Conditions			Tissue		
Taxon	Species	Oil/Hydrocarbon	Max. Conc. (ppm)	Time (days)	Concentration (ppm)	Conc. Factor	Reference
		Water					
Crustaceans	*Penaeus aztecus* (Postlarval)	No. 2 fuel oil, WSF (total naphthalenes)	0.85	0.2	55	65	Anderson 1977
					25	29	
	Palaemonetes pugio	No. 2 fuel oil, WSF (total naphthalenes)	0.1	0.2	2	20	Anderson 1977
	Penaeus setiferus	No. 2 fuel oil, Field experiment (total napahthalenes)	0.3	2	60	200	Cox et al. 1975
			0.3	3	19	63	
	Hippolyte clarkii	Prudhoe Bay, WSF (naphthalenes and phenanthrenes)	1.0	1	18	18	Anderson et al. 1980
			0.6	2	30	50	
			0.4	3	30	75	
	Pandalus danae	Prudhoe Bay, WSF (naphthalenes and phenanthrenes)	0.8	0.3	20	25	
			0.5	1	10	20	
			0.3	3	5	17	
	Uca minax	No. 2 fuel oil, Field experiment (total naphthalenes)	0.3	3	22	74	Cox et al. 1975
	Sesarma cinereum	No. 2 fuel oil, Field experiment (total naphthalenes)	0.3	3	32	106	Cox et al. 1975
	Anonyx laticoxae	Prudhoe Bay, WSF (total naphthalenes)	0.120	1	10	83	Anderson et al. 1979
			0.160	1	10	62	
			0.031	4	2	64	
			0.022	7-15	25	1136	

TABLE 6. SUMMARY OF AROMATIC HYDROCARBON UPTAKE BY MARINE ORGANISMS (CONTINUED)

		Exposure Conditions			Tissue		
Taxon	Species	Oil/Hydrocarbon	Max. Conc. (ppm)	Time (days)	Concentration (ppm)	Conc. Factor	Reference
		Sediment					
	Anonyx laticoxae		2	4	8	4	Anderson et al. 1979
		Water					
Polychaetes	*Neanthes arenaceodentata*	No. 2 fuel oil, WSF (total naphthalenes)	0.6	1	12	20	Rossi & Anderson 1977a
		Sediment (total naphthalenes)	10	28	<0.1	0	Rossi 1977
		Food Methylnaphthalene)	0.05	16	<0.1	0	
		Sediment					
	Abarenicola pacifica	Prudhoe Bay					
		Phenanthrene	5.1	60	0.28	1-4	Augenfeld et al. 1982
		Chrysene	0.2	58	1.1	1-6	
		Benzo(a)pyrene	0.08	60	0.17	1-6	
		Water					
Fish	*Fundulus similus*	No. 2 fuel oil, WSF (total naphthalenes)	1.9	0.2	Liver 4,481	2,358	Dixit & Anderson 1977
					Gall Bladder 66,704	35,107	
					Heart 9,714	5,113	
					Brain 2,387	1,256	

TABLE 6. SUMMARY OF AROMATIC HYDROCARBON UPTAKE BY MARINE ORGANISMS (CONTINUED)

Taxon	Species	Exposure Conditions		Time (days)	Tissue		Reference
		Oil/Hydrocarbon	Max. Conc. (ppm)		Concentration (ppm)	Conc. Factor	
		Water (con't.)					
Fish	Salmo gairdneri	^{14}C-naphthalene	0.005	1	Bile fluid 2.1	415	Melancon & Lech 1978
			0.005	0.3	Total body 0.3	60	
			0.023	0.3	Total body 2.9	126	
			0.5	1	Bile 36	71	
		^{14}C-2 methyl-naphthalene	0.005		Bile 13	2,566	Lee et al. 1972
			0.5	1	Bile 109	218	
	Gillichthys mirabilis	^{14}C-Benzo(a)pyrene	0.001	4	Liver 0.01	10	
					Flesh 0.002	2	
					Heart 0.03	30	
					Gall bladder 7.4	7,400	
		^{14}C-naphthalene	29	0.04	Liver 2200	76	
					Flesh 9100	314	
					Heart 2500	86	
					Gall Bladder 4,200	145	
		Sediment					
	Parophyrs vetulus	Alaskan North Slope crude oil (aromatics)	3	27	Liver 4	1.3	McCain et al. 1978
				51	Liver 0.18	0.1	

Bioconcentration factors for PAH in marine crustaceans exposed via the water usually fall in the range of 2 to 200. When the amphipod Anonyx laticoxae was exposed to a water-soluble fraction of Prudhoe Bay crude oil for 7 to 15 days, the bioconcentration factor for total naphthalenes reached 1,136 (Anderson et al., 1979). When exposed to oil-contaminated sediments for four days, the same species reached a maximum bioconcentration factor of only 4.

Polychaetes (Neanthes arenaceodentata) accumulated naphthalenes to a concentration 20 times that in the ambient medium when exposed to a water-soluble fraction of a light crude oil (Rossi and Anderson, 1977a). When fed oil-contaminated food or exposed to oil-contaminated sediments, the same species failed to accumulate significant concentrations of naphthalenes (Rossi, 1977). On the other hand, the deposit-feeding polychaete, Abarenicola pacifica, accumulated three PAH from sediments to bioconcentration factors of 1 to 6 during exposure to the sediments for up to 60 days (Augenfeld et al., 1982).

A majority of bioaccumulation studies of PAH in marine fish have been performed during brief exposures to the hydrocarbons in the water. Under these conditions, fish typically show bioconcentration factors for PAH in different tissues in the range of about 100 to 1,000. The gall bladder, a major route of PAH excretion in fish, may exhibit a transitory bioconcentration factor of up to about 35, 000, reflecting rapid excretion of accumulated hydrocarbons. If the duration of exposure is extended beyond a few days, bioconcentration factors for PAH in fish drop precipitously, due to induction of the mixed function oxygenase system, leading to rapid metabolism and excretion of PAH. However, high concentrations of PAH metabolites may remain bound to and undetected in the tissues (Malins et al., 1982). As a result of this process, marine fish from sites heavily impacted by an oil spill may contain low concentrations of unmetabolized PAH in their tissues (Neff and Haensly, 1982).

Accumulation and release of PAH by marine animals from Alaska exhibit patterns similar to those described for marine animals generally (Rice et al., 1984). Figure 9 summarizes results of experiments in which four species of Alaskan marine animals were exposed to the water-soluble fraction of Cook Inlet crude oil for 96 hours. The crustaceans accumulated the highest concentrations of aromatic hydrocarbons, followed in order by pink salmon fry and scallops. The pink salmon fry began depurating aromatic hydrocarbons, probably by metabolic degradation, with 24 hours of the start of exposure. The other species depurated the accumulated hydrocarbons rapidly when returned to clean seawater. The scallops depurated most slowly. Three-hour bioconcentration factors in pink salmon fry for aromatic hydrocarbons increased with increasing molecular weight, in the series from toluene to trimethylnaphthalene (Table 7).

Juvenile king crabs, Paralithodes camtschatica, were able to accumulate aromatic hydrocarbons from both water and sediments contaminated with Cook Inlet crude oil (Rice et al., 1983). They accumulated a maximum of 7 and 3000 ppm total aromatics in muscle and hepatopancreas, respectively, during exposure for 28 days to a water-soluble fraction of oil containing 0.5 ppm

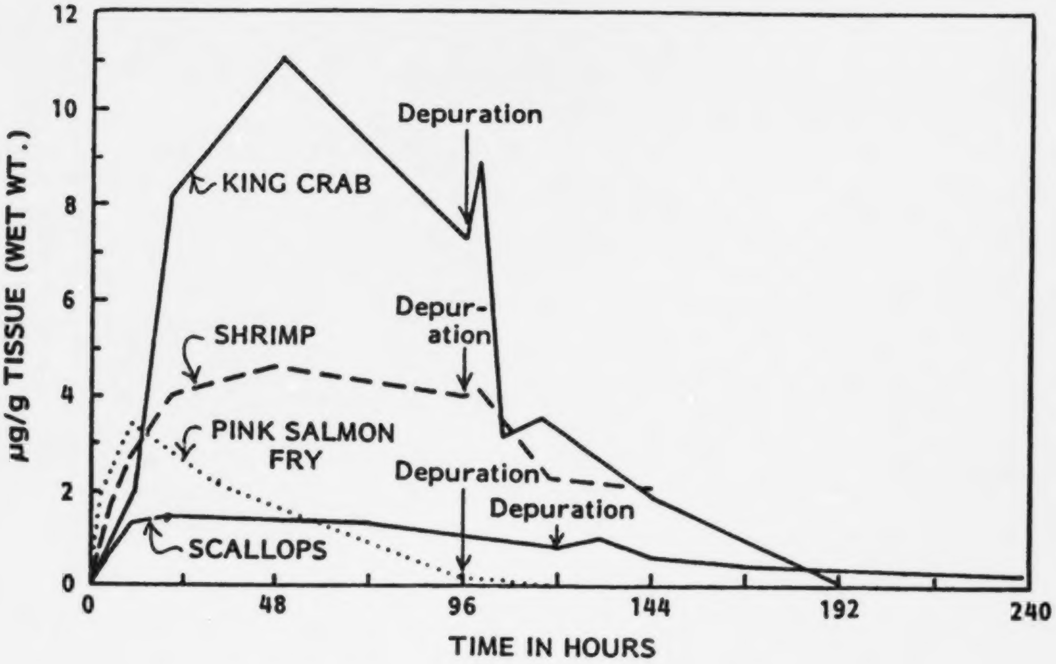


Figure 9. Concentrations of aromatic hydrocarbons in pink shrimp, pink scallops, pink salmon fry, and king crab during exposure to the water-soluble fraction of Cook Inlet crude oil and during subsequent depuration. Points on the graph represent the sum of all aromatic hydrocarbon concentrations found in groups of five individuals determined at various time intervals (from Rice et al., 1984).

TABLE 7. THE EFFECT OF MOLECULAR WEIGHT ON THE ACCUMULATION OF AROMATIC HYDROCARBONS BY PINK SALMON. THE BIOCONCENTRATION FACTOR IS THE RATIO OF TISSUE CONCENTRATION TO WATER CONCENTRATION AFTER 3 H EXPOSURE TO THE WSF OF COOK INLET CRUDE OIL (From Rice et al., 1984).

Oil Component	Bioconcentration Factor
Toluene	3
Naphthalene	64
Methylnaphthalene	139
Dimethylnaphthalene	198
Trimethylnaphthalene	380

total aromatics. Maximum concentrations were reached in muscle after one day and in hepatopancreas after four days. During exposure to sediments containing two percent Cook Inlet crude oil for 90 days, the juvenile crabs accumulated up to 3 ppm and 370 ppm total aromatics in muscle and hepatopancreas, respectively. Maximum accumulations were reached after 10 and 90 days, respectively.

DISTRIBUTION OF ACCUMULATED PAH IN ANIMAL TISSUES

Studies of PAH bioaccumulation in bivalve molluscs usually have not included determinations of the distribution of accumulated hydrocarbons in the tissues. The visceral mass, including the digestive gland, constitutes most of the body mass, and most consumers of bivalves, including man, ingest the entire soft tissues. However, Neff and Anderson (1975) demonstrated that when the marsh clam Rangia cuneata was exposed to ^{14}C-labelled benzo(a)pyrene (BaP) in the water, approximately 50 percent of the radioactivity accumulated was in the viscera. Mantle tissue contained the second highest concentration, and the remainder of the BaP was distributed evenly among the remaining tissues. More recently, Widdows et al. (1982) reported that the concentration of accumulated aromatic hydrocarbons in Mytilus edulis was approximately five times higher in the digestive gland than in other tissues.

Figure 10A shows the distribution of total naphthalenes in body parts and organs of the brown shrimp Penaeus aztecus during and following exposure to the water-soluble fraction of No. 2 fuel oil. The digestive gland accumulated naphthalenes to the highest concentration during exposure and retained them longest during depuration. Similar results were obtained n spot shrimp, Pandalus platyceros, an Alaskan species (Sanborn and Malins, 1980). During exposure to a water-soluble fraction of Prudhoe Bay crude oil, thorasic segments, including digestive gland accumulated about four times more aromatic hydrocarbons than abdominal segments. Similarly, in purple shore crabs, Hemigrapsus nudus, maximum bioconcentration factors for naphthalene ranged from 4.2 in hemolymph to 104 in digestive gland (Rice et al., 1984).

In fish distribution of accumulated PAH seems to be somewhat more uniform (Figure 10B). Greatest accumulation is in gall bladder and digestive tract, major routes of PAH excretion. Brain, probably because it is high in lipids, also tends to accumulate high concentrations of PAH. This may have important implications relative to the mode of toxic action of PAH. Research in Malins' laboratory with marine fish from the Pacific Northwest and Alaska (e.g., Roubal et al., 1971; Collier et al., 1978; Varanasi et al., 1981) also revealed significant bioaccumulation of PAH in liver gut and brain. Whereas, much of the PAH in liver was present as metabolites, most of that in brain tissue was unmetabolized.

RELEASE OF PAH

A majority of the depuration studies have been conducted in very clean seawater, not environments where levels of contamination slowly decrease.

FIGURE 10. TISSUE DISTRIBUTION OF NAPHTHALENES.

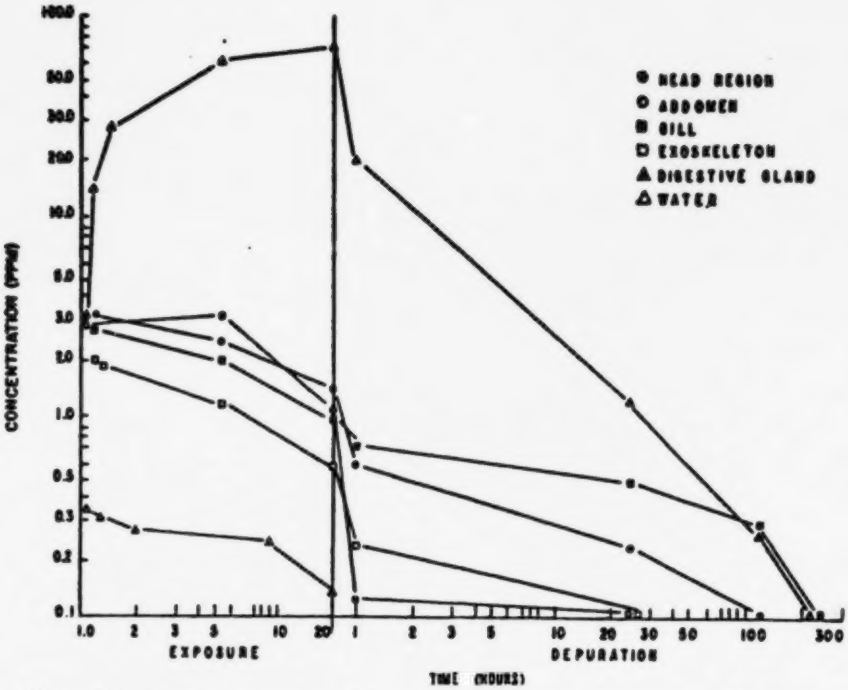


Figure 10A. Penaeus aztecus. Accumulation and retention of total naphthalenes by different body regions of juvenile brown shrimp exposed to 20% dilution of water-soluble fraction of No. 2 fuel oil. Body regions of 3 shrimp were pooled for each data point, and background values were subtracted. (From Neff et al. 1976b).

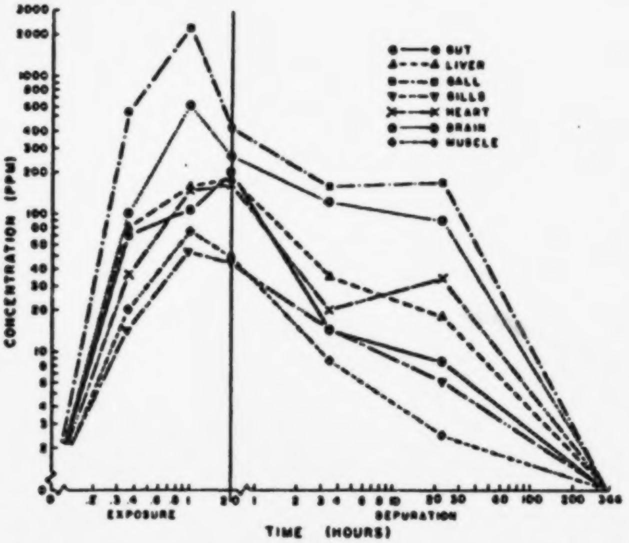


Figure 10B. Fundulus similis. Distribution of total naphthalenes in various tissues of Gulf killifish during exposure to water-soluble fraction of No. 2 fuel oil and at different times following exposure. Water-soluble fraction contained approximately 2 ppm total naphthalenes. (From Neff et al., 1976b).

In the natural environment, the reservoir of contaminants in sediments may continue to provide low levels of bioavailable petroleum components, even after the sources of input have been removed.

Data from various studies on the depuration of hydrocarbons in marine organisms were fit to a hyperbolic kinetic model. To compare experiments using different exposure concentrations, the data were normalized to percent of the original hydrocarbon in the animals at time 0 (i.e., before depuration began). The data were then transformed to linear form and regression statistics calculated. Thus:

$$P = t/b + at \text{ or } 1/P = \frac{b}{t} + a$$

where t = time (days)
a = constant
b = coefficient
P = percent remaining

This hyperbolic model has a demonstrated physical basis in equilibrium modeling both in adsorption chemistry as the Langmuir equation (Browman and Chesters, 1977) and in the Michaelis-Menten model (Segel, 1976). It has been used to model the bioaccumulation and depuration of organic compounds from synthetic fuel residuals (Hardy et al., 1985a) and the flux of metals through water surfaces (Hardy et al., 1985b). The time at which 50% of the original hydrocarbon remains is estimated by substituting 50 for P in the above equation and solving for t. Care must be taken in any attempt to estimate the percent remaining at longer periods since this model does not fit well the slow rates of release occurring in bivalves after about 10 days of depuration (Neff and Anderson, 1981).

A major distinction must be made between saturates or n-paraffins and aromatic hydrocarbons. Saturates have in general been found to produce substantially less toxicity for marine species than aromatic hydrocarbons (Neff, 1979). At similar molecular weights, saturates are less soluble in seawater than aromatics and their uptake is frequently associated with the intake (through filtering) of oil droplets. Other important factors to consider are the relative partitioning of different hydrocarbons from lipid pools in the tissues back to seawater and the rates of metabolic conversion of aromatic hydrocarbons to degradation products within different marine species.

Table 8 shows that the half-life (t_{50}) of total hydrocarbons and naphthalenes in bivalves is on the order of 5 days. The faster depuration shown for n-paraffins is likely the result of the removal of oil particles (droplets) associated with the external portions of membranes as compared to soluble components (aromatics) which have entered the tissue. Published curves for depuration and tables of tissue content consistently show a rapid decline in bivalve body burdens shortly after transfer to clean water (Neff, 1979; Neff and Anderson, 1981). This rapid 50% loss is followed by a slower

TABLE 8. SUMMARY OF DEPURATION KINETICS FOR PETROLEUM HYDROCARBONS

Hydrocarbons (organisms)	Coefficient (b)	Constant (a)	n[1]	r[2]	t50[3]	References
n-paraffins (bivalves)	10141	-7264	12	0.98	0.72	Clark & Finley 1975 Neff et al. 1976b
total hydrocarbons (bivalves)	0.117	-0.339	4	0.96	3.5	Stegeman & Teal 1973
total naphthalenes (bivalves)	0.030	0.048	32	0.93	4.8	Anderson 1973 Neff et al. 1976b Cox et al. 1975 Anderson & Neff 1976 Fucik et al. 1977 Anderson 1977
phenanthrene (bivalves)	41.29 (x10^{-3})	-7.74 (x10^{-3})	11	0.98	0.4	Neff et al. 1976a Neff et al. 1976b
BAP (bivalves)	0.83	-3.61	7	0.89	4.5	Neff & Anderson 1975
BAP II (bivalves)	0.025	-0.016	5	0.95	3.2	Neff et al. 1976a Lee et al. 1978
naphthalenes (shrimp, amphipods and annelids)	0.241	0.056	29	0.89	0.3	Cox et al. 1975 Anderson & Neff 1976 Anderson 1977 Anderson et al. 1979 Anderson et al. 1974b Rossi & Anderson 1977a
naphthalenes (fish)	5.177	-3.341	9	0.99	0.7	Anderson & Neff 1976 Anderson et al. 1974b

[1] n = number of data points.
[2] r = regression coefficient.
[3] t50 = half-life in days.

release, often requiring up to 50 days for complete depuration of petroleum components. The slow release phase is generally explained by a gradual partitioning of the sequestered hydrocarbons from a more stable pool to gill surfaces and release by seawater flushing. A portion of this slow release may be associated with a very low rate of organic hydrocarbon metabolism (aryl hydrocarbon hydroxalase) reported for bivalves. Regardless of the mechanisms, clearly bivalves reach some of the highest bioaccumulation levels for petroleum components and release this material more slowly than most other marine species.

From Table 8 it appears that there are no major differences in the rates of release of petroleum hydrocarbons exhibited by worms (annelids), shrimp, amphipods and fish (t_{50} = 0.3 - 0.7). Since these species possess greater capabilities for enzymatic degradation of petroleum components than bivalves (Section 4 of this report), the final portion of the depuration curves generally exhibit a steeper slope than in bivalves. It is possible to compare the t_{50} values in Table 8 to specific studies conducted in Alaska. Korn and Rice (1981) measured the uptake and depuration rates of naphthalene in early life stages of Coho salmon. Figure 11 shows the uptake by eggs, alevins and fry reached maximal values at different times but approximately the same concentration range (50-100 times exposure concentration). Depuration rates increased with the age of the life stage from egg to fry. The t_{50} value of 0.7 days shown in Table 8 for *Fundulus similis* is very near the t_{50} value for Coho salmon fry (Figure 11). An approximate time to complete removal of tissue contamination by adult polychaetes, shrimp and fish might be 5 to 7 days. Therefore, the time for complete depuration of PAH from bivalves is about an order of magnitude greater than the time required by many other marine species.

When petroleum contamination impacts a coastal zone, hydrocarbon concentrations do not merely reach a peak and sharply decrease to nondetectable levels. For this reason the experimental depuration studies reviewed above may represent the best case for removal of PAH contamination from tissues. In most spill situations and in regions receiving multiple or constant oil inputs, sediments generally become contaminated. Leaching of hydrocarbons from the substrate produces low-level water contamination (including pore water) which may be reflected in an apparent slower depuration rate by infaunal, epifaunal, and demersal species.

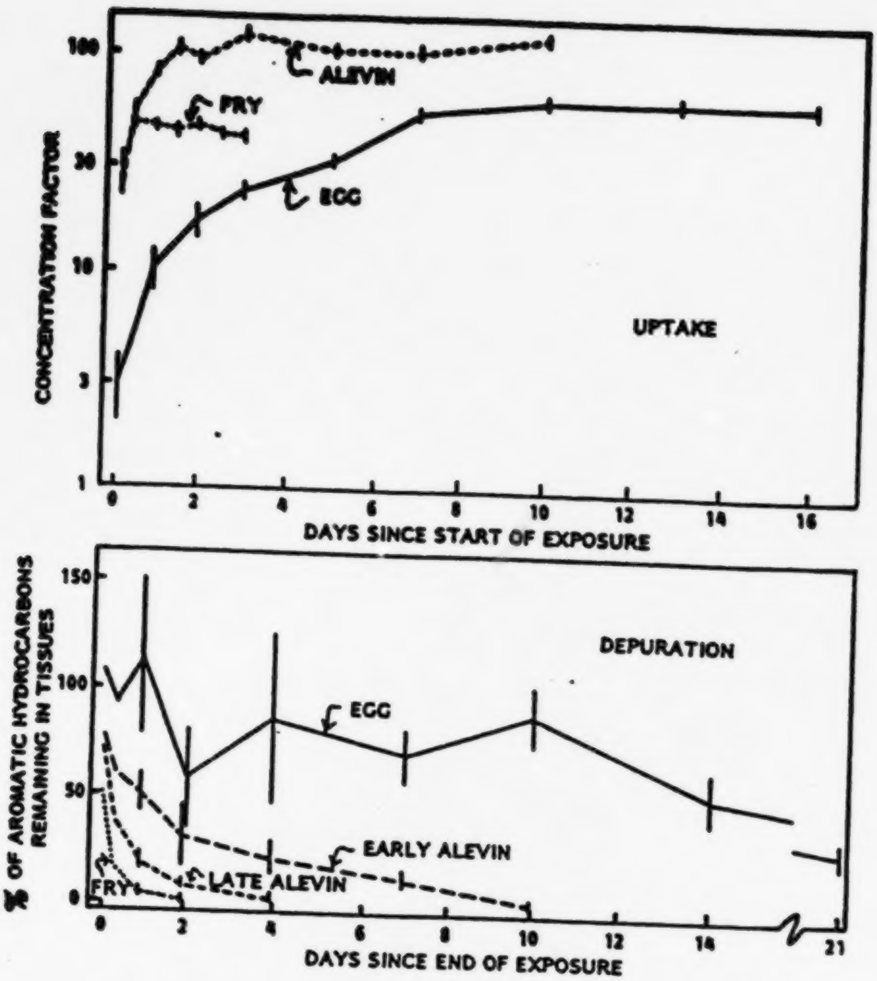


Figure 11. Accumulation and depuration of naphthalene in early life stages of Coho salmon. Fish were exposed to 100 mg/L naphthalene then placed in flowing seawater for depuration. (From Korn and Rice 1981).

FACTORS CONTROLLING THE UPTAKE AND RELEASE OF PAH

The parent compound naphthalene (2 aromatic rings) and alkylbenzenes are generally not retained long on surface sediments due to relatively high water solubility (Roesijadi et al., 1978). Studies conducted with sediments or detritus generally have shown that naphthalenes are not accumulated by organisms exposed to oiled substrates (Rossi, 1977; Roesijadi et al., 1978; Anderson et al., 1978). With increasing molecular weight of aromatics, there is also an increase in the net accumulation within detritivores such as the clam, Macoma inquinata (Table 6). When this species was exposed to oiled sediments containing relatively high concentrations of those ^{14}C-labeled PAH, bioaccumulation was quite low. Time of exposure of benthic species to contaminated sediments and the molecular weight of the specific hydrocarbon measured are probably the most important factors regulating the final level of tissue accumulation.

There is increasing evidence indicates that persistence of specific hydrocarbons in sediments, in the absence of new inputs, is dependent upon the interaction of chemical, physical and biological factors. Lower molecular weight aromatics (naphthalene and smaller) tend to be both degraded (by sediment-associated microorganisms) and leached (water and sediment movement) more rapidly than higher molecular weight components. As these compounds are released from surficial sediments they may be taken up by benthic species, where similar degradative pathways and seawater flushing gradually serve to decrease body burdens. In temperate waters, this cycle of events may take place rather rapidly, so that animals in the natural environment exposed to single inputs of lower molecular weight compounds may not show significant tissue contamination after one to two months of sediment exposure. Long-term field experiments with contaminated sediments have been used to verify these assumptions. To our knowledge this approach has not been applied in Alaskan coastal environments. Just the opposite pattern in bioaccumulation is expected if a constant discharge of petroleum components is taking place. Naphthalene and alkylnaphthalenes are among the compounds that are bioconcentrated to the greatest extent in tissues of most marine species (Table 6) exposed to soluble hydrocarbons.

Examination of data summarized in Table 6 on alkylnaphthalenes, phenanthrenes, chrysene and benzo(a)pyrene lead to the conclusion that these PAH behave quite differently, but predictably, when organisms are exposed to contaminated sediments. For example, when the reservoir (total concentration) in sediment is sufficiently high (5-10 ppm), benthic species may accumulate alkylnaphthalenes and phenanthrenes from sediment in periods of one to two months (Roesijadi et al., 1978; Augenfeld et al., 1982). Surficial sediments release the majority of these components to the water during this period, but lower layers of contaminated material may continue releasing significant amounts, which are available for infauna. These intermediate molecular weight compounds are also available from solution in constant discharges, but their concentrations are generally quite low. As in the case of naphthalene, these PAH can be accumulated in organisms to sufficiently high concentrations to produce mortality and sublethal effects (Anderson et al., 1980). Because of the slower release rates from sediments (compared to the parent compound), alkylnaphthalenes and phenanthrenes can also exert a significant sublethal effect from contaminated sediments.

Chrysene and benzo(a)pyrene and other petroleum components in the same molecular weight range have very low water solubility and have not been shown to either reach high concentrations in discharges or to produce significant mortality for marine species (Rossi and Neff, 1978). While there is potential for producing carcinogenic or mutagenic responses in marine species, clear evidence of this type of impact still is circumstantial. Varanasi et al. (1982a, b) and Varanasi and Gmur (1981) provide evidence of the manner by which English sole metabolize B(a)P and the occurrence of covalent binding of metabolites to macromolecules. While such a pathway may well lead to impacts on populations, including cancer, cause and effect relationships in the environment are difficult to document. Primary concern regarding high molecular weight PAH has been the contamination of marine organisms exposed to polluted sediments and transfer to higher organisms in the food web. Since the 4- and 5-ring aromatics partition very slowly from sediments to interstitial water and the overlying water column, sediments represent a relatively stable reservoir for the bioaccumulation by infaunal species. Low solubility makes uptake from seawater (discharges) unlikely, but organisms in close contact with sediments may continuously accumulate the low levels of these components slowly released from particles to the interstitial water. The rate of uptake by organisms is therefore very slow but continuous, and periods of 30 to 60 days may not be long enough to accurately assess the magnitude of bioaccumulation (Augenfeld et al., 1982). Foodchain transfer of contamination to predators is possible, but for reasons discussed in Section 4, the turnover of PAH in predators is such that biomagnification has not been shown.

In summary, rapid uptake, particularly from water, characterizes the movement of naphthalene from the environment to marine species and toxic effects may be produced. Alkylnaphthalenes and phenanthrenes occupy an intermediate molecular weight range, such that uptake and effects occur over a longer period from sediment exposures. If a marine discharge produces levels in the receiving water between 0.2 and 1.0 ppm of these compounds, acute toxicity is possible. A more likely event is the chronic sublethal effect on infauna from long-term exposure to contaminated sediments. Higher molecular weight compounds, including chrysene and benzo(a)pyrene are less likely to produce acutely toxic effects on the infauna, but gradual tissue contamination is possible.

RELATIONSHIPS BETWEEN TISSUE CONTAMINATION BY PAH AND EFFECTS

There are relatively few studies describing the level of PAH contamination associated with acute or sublethal effects on marine species. A primary reason for our lack of information in this area is that sensitive species are generally used in toxicity tests. These often small and fragile animals may not withstand longer exposure times and if they do, the small amount of tissue may not lend itself to detailed chemical analyses.

Bivalves, which are the best species for demonstrating bioaccumulation, are generally not the most sensitive organisms for use in assessing toxicity.

During flowing exposure tests with either a seawater extract of Prudhoe Bay crude (PBC) oil or chemically dispersed PBC, Anderson et al. (1980; 1984; 1985) have used the shrimp (Pandalus danae) to determine the relationship between toxicity and body burdens. With different exposure systems (WSF or dispersed oil) and varying periods of exposure to different concentrations, they have found that a tissue level of 8 to 13 ppm total naphthalenes and phenanthrenes correlates with 50% mortality in Pandalus danae. Stekoll et al. (1980) described the sublethal effects of chronic oil exposure on the clam, Macoma balthica and coworkers (Clement et al., 1980) characterized the extent of bioaccumulation. Clams exposed to 0.03 ppm total hydrocarbons for 60 to 120 days contained aromatic hydrocarbons between 12 and 16 ppm. Tissue concentration factors increased with increasing substitution of the parent aromatic ring structure for naphthalenes, dibenzothiophenes, anthracenes and chrysenes. At the 60-day exposure to 0.03 ppm, the clams exhibited a negative energy balance, which the authors conclude would lead to population decreases. Widdows et al. (1982) reported on an extensive study of the sublethal effects of oil exposure on the mussel, Mytilus edulis. The study demonstrated the correlation between tissue content of aromatic hydrocarbons and the magnitude of suppression in energy balance (scope for growth). At tissue levels above 7 ppm aromatic hydrocarbons, there was either zero or negative scope for growth and higher concentrations produced greater reductions in energy balance.

Roesijadi and Anderson (1979), Augenfeld et al. (1980) and Anderson et al. (1983) have shown that when the bivalves Protothaca staminea and Macoma inquinata contain levels of PAH at 1 to 4 ppm, sublethal effects are demonstrated. Since these studies were all conducted for one month or more in contaminated sediments, it is likely that animals contained higher levels of at least naphthalenes during earlier periods of exposure. The impacts observed were probably the result of both short-term high concentrations of naphthalenes and longer exposures to the higher molecular weight compounds.

ALASKAN PERSPECTIVE

Alaskan marine animals, like those from temperate and tropical climates, readily accumulate PAH and related hydrocarbons from water. Bioconcentration factors (concentration in tissue/concentration in medium) tend to be higher for bivalve molluscs than for other taxa of marine animals. Accumulation of PAH from sediment is less efficient than from the water. However, for medium molecular weight aromatics, alkyl naphthalenes, phenanthrenes and dibenzothiophenes, sediments may be a major source of chronic contamination of benthic and demersal species.

Low temperatures, characteristic of Alaskan coastal waters, do not seem greatly to affect the rate of accumulation and release of hydrocarbons by marine animals. Rate of PAH bioaccumulation may be increased in some species such as bivalve molluscs and decreased in others such as fish by low water temperatures. In addition, low water temperatures tend to decrease the rate of metabolism and excretion of PAH in those species which depend heavily on the mixed function oxygenase system for PAH metabolism (Rice et al., 1984). This slower rate of depuration plus the greater persistence of PAH in low temperature marine environments, may mean that the potential for chronic impacts of PAH pollution of the Alaskan marine environment is greater than for more temperate and tropical climates.

6. BIOLOGICAL EFFECTS OF PAH

Over the past 5 years, extensive research has been performed world-wide to determine the potential effects of petroleum hydrocarbons on species, populations and communities of marine animals. Recently, a review of Oil in the Sea was published by the National Academy of Sciences (NAS, 1985). Both short-term (acute) toxicity tests, designed to estimate the concentration causing 50 percent mortality in one to a few days (LC_{50}), and short- or long-term tests designed to detect other responses than mortality, have been performed with oil or specific PAH and a wide variety of marine organisms. Collectively, investigations concerning a biological response other than death have been referred to as sublethal studies and include the detection of abnormal biochemical, physiological, histological, developmental, reproductive or behavioral responses in a single species, at PAH concentrations not producing significant mortality. This section will attempt to summarize both acute and sublethal responses, with emphasis on studies conducted with Alaskan species. It should be noted, however, that the majority of studies dealing with the acute toxicity or sublethal effects of oil and specific PAH in marine organisms have been conducted in the lower 48 states. All of these findings relate to Alaskan species since the basic physiologv of organisms and chemical-physical alterations of oil in water are generically similar throughout the marine environment. It is fortunate that the Auke Bay National Marine Fisheries Service Laboratory has recently produced a review of their oil-effects research (Rice et al., 1984). The majority of this type of research in Alaska has been conducted by these investigators, and their findings are included in this report.

TOXICITY OF SPECIFIC COMPOUNDS

The fact that oils, and especially their water-soluble fraction (WSF), vary in the proportion of monoaromatics and higher molecular weight diaromatics and triaromatics, led researchers to investigate the toxicity of specific petroleum to a variety of marine organisms. Figure 12 illustrates the concentrations of specific aromatic hydrocarbons required to produce 50% mortality in 96 h (96 h LC_{50}) or 24 h (24 h LC_{50}) for a range of organisms. The general trend is an increase in acute toxicity (lower LC_{50} value) as molecular weight increases to the highest molecular weight compound (fluoranthrene) found to produce acute toxicity. Unfortunately, there is no complete data set for any one species. The shrimp, Palaemonetes pugio, was tested with the low to medium range of molecular weight aromatics (benzene- phenanthrene), while the polychaete, Neanthes arenaceodentata, was tested with PAH of medium to high molecular weight [naphthalene - dibenz(a)anthracene]. Data for other species are mostly for

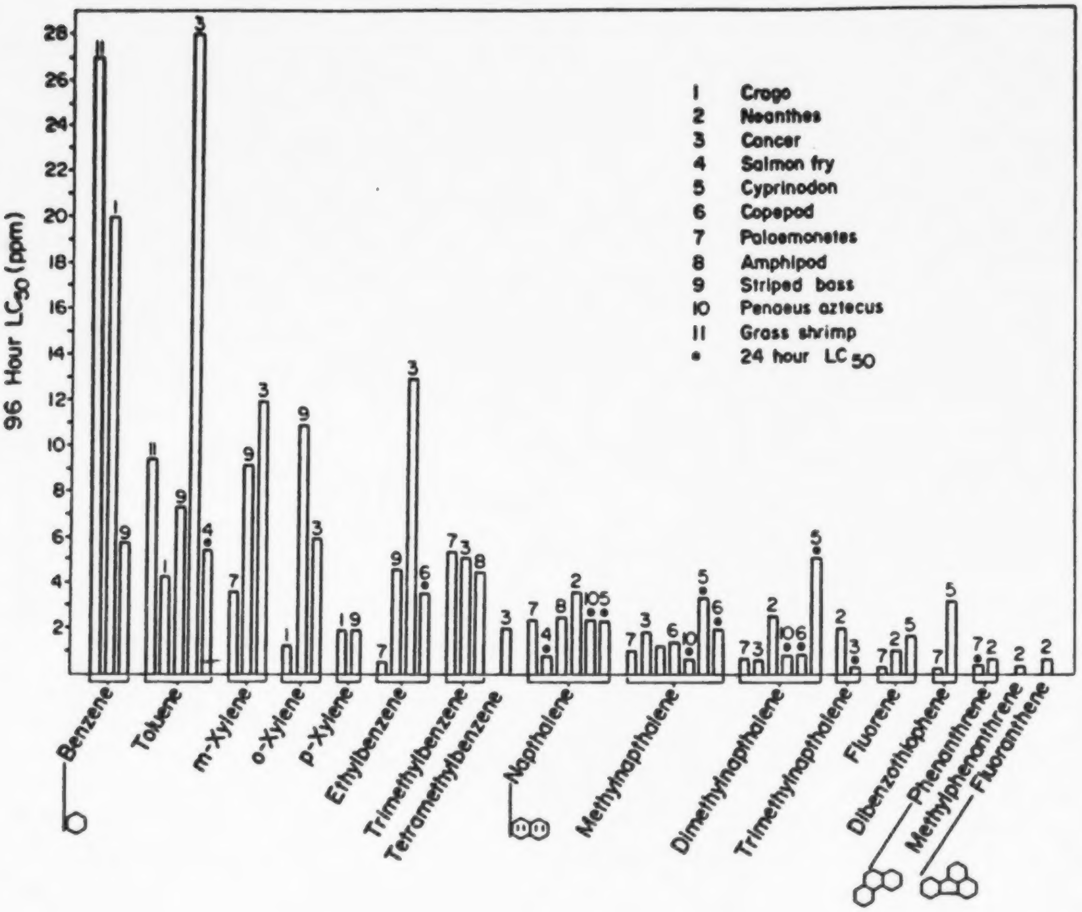


Figure 12. Concentrations of specific petroleum compounds producing 50% mortality for selected marine organisms (Data from Caldwell et al., 1977; Benville and Korn, 1977; Neff et al., 1976a; Thomas and Rice, 1979; Young, 1977; Rossi and Neff, 1978; Ott et al., 1978; and Lee and Nicol, 1978).

various intermediate molecular weight compounds. Therefore, individual species may not necessarily follow the general trend.

The inverse relationship between molecular weight and acute toxicity of aromatics in the series from benzene to fluoranthene may be attributed in part to the fact that the lower molecular weight aromatics are volatile and are lost rapidly from bioassay media, decreasing their apparent toxicity. In addition, as Hutchinson et al. (1980) have shown, the degree of membrane perturbation, and thus the toxicity of an aromatic hydrocarbon, will be proportional to the concentration of the hydrocarbon associated with the membrane surface. This, in turn, will be proportional to activity (product of mole fraction and activity coefficient) of the aromatic hydrocarbon in the aqueous phase. Since the activity coefficient is inversely proportional to solubility, less soluble (higher molecular weight) aromatics should have a greater effect at a given concentration than more soluble ones.

TOXICITY OF OIL EXTRACTS

It is important to understand the interaction of oil and seawater in producing an extract of soluble petroleum components and to determine the rates these compounds are dissipated from both oil and oil-and-water phases. In the laboratory, water-soluble fractions (WSF) of oil have been made by slowly mixing one part oil over nine parts seawater for 20 hours (Anderson et al., 1974a). Table 9 shows the relative contribution of different aromatics to several oil extracts (WSF). The percentage of n-paraffins in the WSF was a very low (1-2%) since they are less soluble than the monoaromatics, which represented about 90% of the WSF. The remaining 4 to 6% is composed of naphthalenes, which are probably the most toxic components. Total concentrations of aromatics in these WSF (10% mixture; oil over water) were from about 6 to 20 ppm, and similar values were obtained when a flowing exposure system was used (Anderson et al., 1980). Weathering of Prudhoe Bay crude oil in the open air over slowly flowing seawater for 24 days resulted in 100% loss of monoaromatics, and naphthalenes were reduced by about 20 to 80%, based on the molecular weight and structure of the specific compound (Riley et al., 1980).

Table 10 demonstrates the major difference between the WSF of the very toxic No. 2 Fuel oil and the WSFs of two crude oils. This table (from Rice et al., 1984) also shows the similarity between treated ballast water and the WSF from crude oils. Naphthalenes are the major components of No. 2 Fuel oil WSF and are 15 to 20 times higher than naphthalenes in water equilibrated with crude oil. These authors have also shown that temperatures between 5 and 15°C have a considerable influence on the rate of loss of aromatic hydrocarbons from test solutions during 96 h. Low temperatures substantially decrease the rate of volatilization of light aromatics from the WSF.

Table 11 from the review of Malins (1977) summarizes the data from numerous toxicity studies. The ranges shown are quite large. Often, results are based on either no chemical analyses or rather poor analytical data. The ranges probably present a reasonable estimate of the concentrations of oil extracts or suspensions of oil required to produce 50%

TABLE 9. THE CONCENTRATIONS OF C_{12}-C_{24} N-PARAFFINS AND AROMATIC HYDROCARBONS IN REFERENCE OILS AND THE 10% WATER-SOLUBLE FRACTIONS (WSFs) PREPARED FROM THEM. Hydrocarbon concentrations in the oils are given as percent (g/100 ml) and in the WSFs as parts per billion (µg/L) in $20^{0}/_{00}$ seawater (from Anderson et al., 1974a,b; and Anderson et al., 1980).

Name of Compound	S. Louisiana		Kuwait		#2 Fuel Oil		Bunker C		Prudhoe Bay	
	Whole Oil (%)	WSF (ppb)	Whole Oil (%)	WSF (ppb)	Whole Oil (%)	WSF (ppb)	Whole Oil (%)	WSF (ppb)	Whole Oil (%)	WSF[1] (ppb)
n-paraffins										
C_{14}	0.44	10	0.46	<0.5	0.82	5.0	0.11	0.8	0.36	[2]
C_{15}	0.48	10	0.41	<0.5	1.06	7.0	0.11	0.9	0.37	
C_{16}	0.54	12	0.43	0.6	1.20	8.0	0.15	1.2	0.36	
C_{17}	0.41	9	0.42	0.8	0.98	6.0	0.12	1.9	0.34	
C_{18}	0.30	7	0.28	0.5	0.60	4.0	0.10	1.0	0.30	
Total C_{12}-C_{24} n-paraffins	3.98	89	4.00	2.9	7.38	47	1.26	12	4.40	2.93
aromatics										
benzene	[3]	6,750	[3]	3,360	[3]	550	[3]	40	[3]	36.1
toluene		4,130		3,620		1,040		80	0.93	55.5
alkylbenzenes[4]		760		730		970		110	3.19	53.8
naphthalene	0.04	120	0.04	20	0.40	840	0.10	210	0.16	1.6
1-methylnaphthalene	0.08	60	0.05	20	0.82	340	0.28	190	0.21	2.4
2-methylnaphthalene	0.09	50	0.07	8	1.89	480	0.47	200	0.25	
dimethylnaphthalenes[4]	0.36	60	0.20	20	3.11	240	1.23	200	0.80	1.4
trimethylnaphthalenes[4]	0.27	8	0.19	3	1.84	30	0.88	100	0.48	0.6
biphenyls[4]	<0.01	2	<0.01	1	0.16	28	<0.01	1	[3]	[3]
fluorenes[4]	0.02	3	<0.01	3	0.36	20	0.24	11	[3]	[3]
phenanthrenes[4]	0.06	4	0.04	3	0.53	20	1.11	23	0.39	0.3
dibenzothiophenes[4]	0.02	1	0.01	1	0.07	4	<0.01	1	0.13[4]	[3]
Total aromatics	0.94	11,948	0.60	7,789	9.18	4,562	4.31	1,166	6.54	151.7
Total hydrocarbons measured	4.92	12,037	4.60	7,792	16.56	4,609	5.57	1,178	10.94	154.6
Total hydrocarbons present (IR analysis)		19,800		10,400		8,700		6,300		141

[1] = $30^{o}/_{oo}$ Seawater extract (not 10%) in a flowing system.
[2] = Individual n-paraffin concentrations were very low.
[3] = Not measured.
[4] = Total of several isomers.

TABLE 10. COMPOSITION OF EXTRACTS FROM CRUDE AND REFINED OILS AND TANKER BALLAST TREATMENT EFFLUENT (FROM RICE ET. AL., 1984).

	Concentration (ppm)			
Component	Prudhoe Bay[a] WSF	Cook Inlet[a] WSF	Ballast[a] effluent	Fuel[b] oil WSF
Benzene	1.8	3.2	3.2	0.11
Toluene	2.0	2.5	2.2	0.17
o-xylene	0.28	0.35	0.32	0.12
m- and *p*-xylene	0.58	0.78	0.68	0.17
Naphthalene	0.084	0.15	0.098	0.15
1-Methylnaphthalene	0.032	0.066	0.049	0.13
2-Methylnaphthalene	0.048	0.088	0.066	0.25
Ratio of all monoaromatic hydrocarbons to diaromatic hydrocarbons	19.3:1	15.7:1	23.6:1	1.1:1

[a] From Rice et al. 1981.

[b] From Rice et al. 1979.

TABLE 11. ACUTE TOXICITY OF PETROLEUM TO MARINE ANIMALS (FROM MALINS, 1977)

Organism	Material Tested	Lethal Concentration
		ppm
Finfish	Soluble hydrocarbons	5-50
Larvae and eggs		0.1-1.0
Pelagic crustacea		1-10
Benthic crustacea		1-10
Gastropods		10-100
Bivalves		5-500
Other benthic invertebrates		1-10
Finfish	No. 2 fuel oil/kerosine	550
Larvae and eggs		0.1-4.0
Pelagic crustacea		5-50
Benthic crustacea		5-50
Bivalves		30,000-40,000
Other benthic invertebrates		5-50
Finfish	Fresh crude oil	88-18,000
Larvae and eggs		0.1-100
Pelagic crustacea		100-40,000
Benthic crustacea		56
Gastropods		?
Bivalves		1,000-100,000
Other benthic invertebrates		100-6,100
Finfish	Gasoline	91
	Diesel fuel	240-420
Finfish	Waste oil	1,700
Larvae and eggs		1->25
Pelagic crustacea		15->50
Finfish	Residual oils	2,000-10,000

mortality after 96 h (4 days) of exposure. Using Alaskan species and Cook Inlet crude and No. 2 Fuel oil, Rice et al. (1979) found that 96-h LC_{50} values for fish, shrimp and crab were from about 1 to 4 ppm total aromatic hydrocarbons. All species were more sensitive to the WSF of No. 2 Fuel oil than the crude oil WSF (Table 12).

Data from studies in Alaska and elsewhere on comparisons between No. 2 Fuel oil and crude oil WSF combined with several studies reviewed by Neff (1979) have led to the conclusion that naphthalenes are very significant contributors to the toxicity of oil extracts. Total naphthalenes include the parent compound naphthalene and analogues with one to four methyl groups attached to the diaromatic ring. Some oils, such as Kuwait, only produce a maximum of 0.07 ppm naphthalenes in the 100% WSF (1:10, oil:water), but South Louisiana and Prudhoe Bay crudes produce maximum naphthalenes concentrations of 0.30 ppm in the WSF. No. 2 Fuel and Bunker C oils produce higher total naphthalenes values (0.90 - 1.93) in the 100% WSF. Table 13 shows the results of toxicity testing with two shrimp species and two polychaetes in Texas (22°C). Toxicity values (LC_{50}) were found to be between 1.7 and 0.3 ppm total naphthalenes, regardless of the type of oil producing the test solution (Anderson et al., 1974a; Rossi et al., 1976). The range of toxic concentrations was relatively small (about five times) for the species tested with four different oils and the values were equivalent to the 100% WSF. Since these concentrations represent a type of equilibrium for a relatively high volume of oil over water, these levels might be present in a spill situation only near the point of oil-seawater mixing.

Also summarized in Table 13 are values for eight species of marine animals (mostly crustaceans) tested in Alaska (4-8°C) which exhibited 96 h LC_{50} at concentrations of about 0.1 to 0.5 ppm total naphthalenes. There is an overlap in the LC_{50} values for all the tests, but somewhat lower values were consistently derived from tests in Alaska at 4 to 8°C, compared with those produced at 22°C. There are two possible explanations for these differences. Organisms living in Alaska may actually be more sensitive. The more likely explanation is that the petroleum components, particularly those of low molecular weight, remained in the exposure solutions for longer periods of time at the lower temperatures. The correct explanation for these differences can be obtained by exposing the organisms to constant concentrations in a flowing system over the same 4-day period.

The findings presented in this section lead to the conclusion that naphthalenes are, perhaps, the most toxic components in the various oils, but that a portion of the toxicity is contributed by some of the monoaromatic compounds present in initially high concentrations in extracts of crude oil. Other important contributors to the toxicity of some crude and refined petroleums are the phenanthrenes and dibenzothiophenes.

TOXICITY OF OIL TO DIFFERENT LIFE STAGES

Figure 13 shows the differences in the tolerances of four species of invertebrates at different life stages to precisely the same extract of No. 2 Fuel oil under the same exposure conditions. For Palaemonetes pugio,

TABLE 12. ACUTE TOXICITY OF WATER-SOLUBLE FRACTIONS (WSF) OF A CRUDE AND REFINED OIL TO ARCTIC MARINE SPECIES FROM FOUR PHYLA*

Organism	Avg. 96-h TLm (ppm) of WSF of:	
	Crude Oil	No. 2 Fuel Oil
Echinodermata		
Sea Cucumber (2 spp.)	10.8	2.3
Mollusca		
10 species	9.8	2.3
Arthropoda		
Crabs (4 spp.) Shrimp (5 spp.)	2.3	2.3
Amphipod, Isopod, Mysid, and Barnacle (1 sp. ea.)	8.5	4.1
Chordata		
Fish (5 spp.)	1.8	1.8

*Data taken from Rice et al. 1977 and 1979.

TABLE 13. CONCENTRATIONS OF NAPHTHALENES IN SPECIFIC OILS PRODUCING 50% MORTALITY FOR SEVERAL MARINE INVERTEBRATES IN 96 HR.

	Kuwait	So. Louisiana	Bunker C	#2 Fuel Oil	Cook Inlet	Prudhoe Bay	Temp.
Palaemonetes[1] *pugio*	[4]	[4]	1.7	1.09	[5]	[5]	22C
Penaeus[1] *aztecus*	[4]	[4]	1.2	1.5	[5]	[5]	22C
Neanthes[2] *arenaceodentata*	[4]	0.32	0.97	0.84	[5]	[5]	22C
Capitella[2] *capitata*	0.28	0.31	0.24	1.51			
Pandalus[3] *goniurus*	[5]	[5]	[5]	(0.16)	0.11 (0.11)	(0.09)	3.5-8C
Crangon[3] *alaskensis*	[5]	[5]	[5]	0.17	0.05		3.5-8C
Paralithodes[3] *camtschatica*	[5]	[5]	[5]	0.48 (0.41)	0.22 (0.20)	(0.20)	3.5-8C
Pandalus[3] *hypsinotus*	[5]	[5]	[5]	[5]	(0.12)	(0.13)	3.5-8C
Pandalus[3] *borealis*	[5]	[5]	[5]	[5]	0.30 (0.09)	(0.13)	3.5-8C
Eualus[3] *fabricii*	[5]	[5]	[5]	0.52 (0.14)	0.11 (0.16)	(0.16)	3.5-8C
Hemigrapsis[3] *nudus*	[5]	[5]	[5]		0.51		
Chlamys[3] *rubida*	[5]	[5]	[5]	(0.20)	(0.16)	(0.17)	3.5-8C

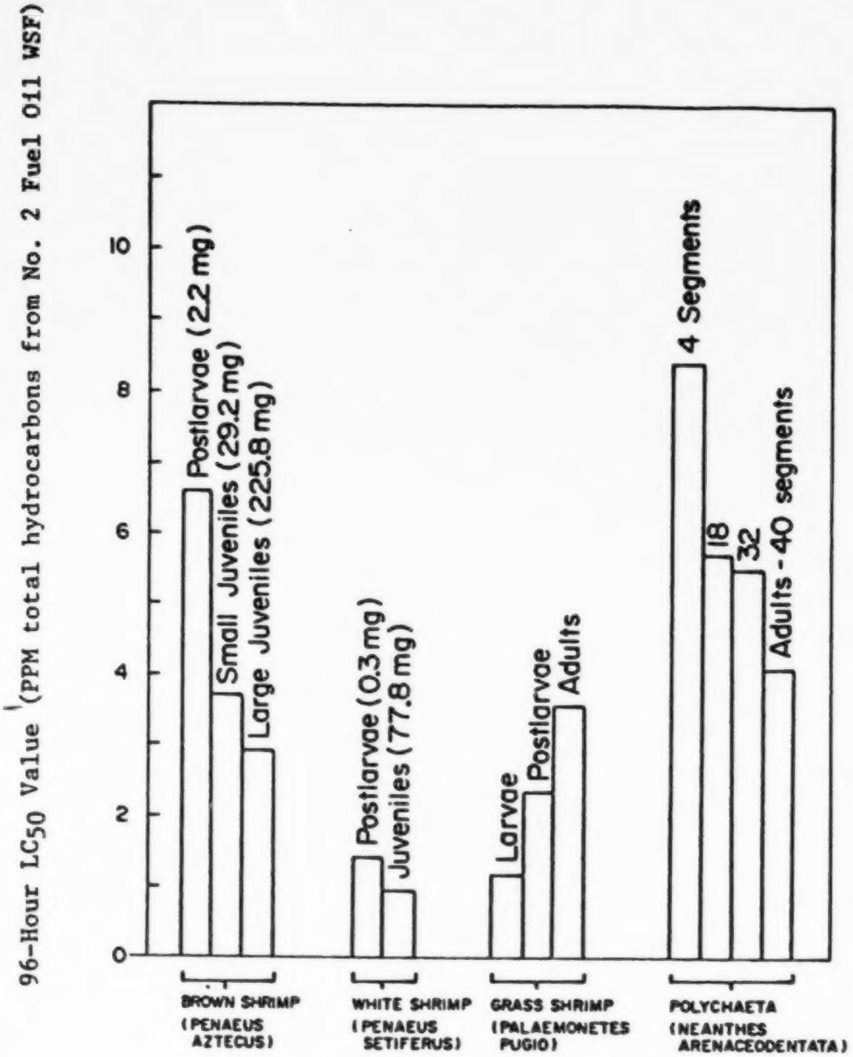


Figure 13. Concentrations of No. 2 Fuel oil WSF producing 50% mortality in 96-h exposures to various life stages of crustaceans and polychaetes (from Neff et al., 1976a and Rossi and Anderson, 1976).

there is a decrease in sensitivity with increase in size and age. However, both Penaeus aztectus and Neanthes arenaceodentata adults are considerably more sensitive to the petroleum extracts than younger stages and sensitivity increases with increasing size.

Few other publications compare the sensitivity of organisms at various life stages (including adults) under exactly the same exposure conditions. Caldwell et al. (1977) and Mecklenburg et al. (1977) discuss the sensitivities of various larval stages of decapod crustaceans. There are particularly sensitive stages in the development of many decapods, including crabs and lobsters (Wells and Sprague, 1976). One should compare the responses of these larval stages to those of the adult large crustaceans in looking at the range of sensitivities. In doing so we often find that the parents are extremely tolerant to oil and are usually resistant to even the highest exposure concentration tested over 4 days. Apparently the large size and relatively impermeable carapace of lobsters and crabs have aided them greatly in their protection from petroleum compounds.

Karinen and Rice (1974) reported impaired molting by crustaceans exposed to crude oil. Mecklenburg et al. (1977) compared animals in various stages of molt. This work and various other observations during toxicity testing, have shown crustaceans are more sensitive at the molt stage than at intermolt periods. Mecklenburg et al. (1977) found that coonstripe shrimp larvae (Pandalus hypsinotus) were approximately eight times more sensitive during molting than during intermolt. There are obviously mechanical and physiological stresses to overcome during molting; also, there is an uptake of the surrounding water which would bring high doses of available contaminants.

In their recent review, Rice et al. (1984) summarized the numerous studies conducted on eggs and larvae of salmon. They noted that eggs and alevins are more tolerant to short-term exposures (96 h) of petroleum hydrocarbons than fry or juvenile salmon. While eggs of Coho and pink salmon are quite resistant to benzene in 96-h tests (LC_{50}=340-540 ppm), the fry of these species exhibited 96-h LC_{50} values of 10 to 15 ppm (Moles et al., 1979). Longer-term exposures of Coho salmon eggs to toluene or naphthalene produced significant reduction in hatching at exposure levels which were less than 1% of the 96-h LC_{50} values for eggs (Korn and Rice, 1981). It should be noted that eggs and fry of most salmon are found in freshwater, but pink salmon often deposit their eggs in regions where temperature and salinity can modify the sensitivity of early life stages of this species. Korn et al. (1979) have found pink salmon fry more sensitive at lower temperatures and there is a general trend of increased sensitivity of salmon fry and smolt with increasing salinity (Moles et al., 1979; Stickle et al., 1982).

Studies at Auke Bay on embryos, larvae and adults of kelp shrimp (Eualus suckleyi) and coonstripe shrimp (Pandalus hypsinotus) showed that eggs were more tolerant to petroleum hydrocarbons than the adult females. Even during long-term exposures (28 d) in a flowing system, the eggs of shrimp survived if the female carrying them survived. Toxicity values for eggs, larvae and adults (96 h and 28 d LC_{50}) were between 0.5 and >1.4 ppm total aromatics. These concentrations are very near the 96-h LC_{50} shown for white shrimp (Penaeus setiferus) in Figure 13. In other Alaskan studies (Brodersen et al., 1977), Stage I larvae of king crab (Paralithodes camtschatica) exhibited 96-h LC_{50} values that were about one-half of the values for juveniles. They also reported an increase of about one order of magnitude (0.2 - 2.0 ppm) in the tolerance of coonstripe shrimp between Stage I and Stage VI larvae.

ACUTE TOXICITY FROM FLOW-THROUGH TESTS

The above findings involved static tests primarily with water-soluble extracts of oil. An extract from a 1:10 (oil:water) mixture produces much the same component distribution as at least one flowing exposure system (Anderson et al., 1980). The tremendous advantage of a flowing system is that component composition does not vary over time of exposure, relative to the volatility of the specific compounds. Thus, flow-through systems provide consistency of exposure, so that either sublethal or lethal responses of organisms can be closely related to specific components and concentrations. Vanderhorst et al. (1976) indicate that flowing exposures may reduce 96-h LC_{50} values to about one-half of static LC_{50} values.

Standard static acute tests are also difficult to interpret because time is rather short (4 days), and time of exposure is not allowed to vary. At least in mortality tests of relatively short (9 days or less) duration, Anderson et al. (1980) found that the time of exposure is as important as concentration. In this study, a 50% mortality of three crustacean species (Pandalus danae, Hippolyte clarkii and Neomysis awatschensis) was predicted by extrapolation of a log-log plot of exposure time (up to 9 days) and concentration of exposure. There was a consistent total hydrocarbon exposure (time x concentration) in ppm-days which produced 50% mortality for these crustacean species. This relationship has been confirmed using Pandalus danae and chemically dispersed oil in constant and diluting exposures (Anderson et al., 1981). More recent data (Anderson, 1984) on Pandalus danae also demonstrate a predictable total exposure producing 50% mortality, regardless of the rate of exposure. Obvious limitations to this approach are very short exposures, which do not provide sufficient time for death (a few hours) or very long exposures to low concentrations (over 9 days), which may allow some animals to accommodate to the petroleum components. Flow-through studies ensure that concentration and composition of the exposures are consistent so that the tolerance of a species can be accurately defined. Impacts on species under realistic spill conditions can be predicted from a knowledge of dilution rates, movement of the organisms and alterations of the hydrocarbons under specific field conditions.

SUBLETHAL EFFECTS

Wolfe (1977) summarized much of the available information on the fate and effects of petroleum hydrocarbons in marine ecosystems with considerable emphasis on Arctic and subarctic environments. In this symposium, Anderson (1977) reviewed studies on physiological, histological, behavioral and reproductive effects of different oil components of several crude and refined oils on marine species (Table 14). While total hydrocarbon values

TABLE 14. SUMMARY OF EFFECTS OF PETROLEUM HYDROCARBONS ON THE GROWTH AND REPRODUCTION OF MARINE ANIMALS (FROM ANDERSON, 1977)

Species	Oil	Exposure (days)	Concentration(ppm)[1]			Growth or Reproduction Parameter	References
			TH	TN	TA		
FISH							
Fundulus similus	So.La.C[2]	20	16.6	0.2	9.7	4% hatch of eggs.	Anderson et al., 1976
Cyprinodon variegatus	No.2 FO[3]	7	2.0	0.6	1.7	0% hatch of eggs.	Anderson et al., 1976
Oncorhynchus gorbuscha	Prudhoe Crude	10	0.7			Reduced growth rate of pink salmon fry.	Rice et al., 1975
DECAPODS							
Cancer magister	Alaskan Crude	60			0.2	Reduced survival of zoeae on longterm exposure.	Caldwell et al., 1977
Rithropanopeus harrasii	No.2 FO	27	1.0	0.3	0.9	Reduced survival and extended development to megalopa.	Neff et al., 1976a
Palaemonetes pugio	No.2 FO	12	0.9	0.3	0.8	Reduced growth rate of larvae.	Tatem, 1977
		3	1.4	0.6		Reduced viability of eggs from exposed gravid females.	
Paralithodes camtschatica	Cook Inlet Crude	1-4	1.6			Inhibition of molting in larvae.	Mecklenburg et al., 1977
Pandalus hypsinotus	Cook Inlet	1-4	1.2			Inhibition of molting in larvae.	
Homarus americanus	Venezuelan	30	0.14			30-day LD_{50} and retarded development of larvae	Wells & Sprague, 1976
AMPHIPODS							
Gammarus oceanicus	Crude	60	0.3-0.4			Reduced growth rate of larvae.	Linden, 1976
POLYCHAETES							
Neanthes arenaceodentata	No.2 FO	22	1.0	0.3	0.9	Reduced growth rate of larvae.	Rossi, 1976
	No.2 FO	28	0.3	0.1		Reduced growth of juveniles by 30%.	Anderson, 1976
Ctenodrilus serratus	No.2 FO	28	2.2	0.5	1.4	Reduced survival and reproduction.	Carr & Reish, 1977
	So.La.C	28	9.9	0.2	7.0		
Ophryotrocha sp	No.2 FO	28	1.3	0.3	0.9		
	So.La.C	28	9.9	0.2	7.0		

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[1] Th, total hydrocarbons; TN, total naphthalenes; TA, total aromatics.

[2] South Louisiana Crude Oil, API reference oil.

[3] High aromatic (38%) No. 2 Fuel Oil, API reference oil.

found to produce abnormal responses varied from 0.1 to 16 ppm, there was closer agreement for both total naphthalenes and total aromatics. A relatively small range of total naphthalenes, 0.1 to 0.6 ppm, adversely affected the growth and reproduction of polychaetes, crustaceans and fish over exposure periods of 1 to 60 days.

Shaw and co-workers (Clement et al., 1980; Stekoll et al., 1980) exposed the clam, Macoma balthica, to a dispersion of Prudhoe Bay crude oil for six months. At the highest concentration (3.0 ppm) of total hydrocarbons, 50% mortality occurred after about 130 days. At the 120-day interval, clams exposed to 0.3 ppm total hydrocarbons exhibited reduced condition index. If the exposure concentration is multiplied times the time in days at the point of significant effect, a total exposure of 36 ppm-days (total hydrocarbons) or 1.2 ppm-days (total aromatics) is derived. The 0.010 ppm measured aromatics (at 0.3 ppm total hydrocarbons) in this study does not include monoaromatics which are likely to be an order of magnitude higher in concentration than other aromatics.

A long-term study with North Sea crude oil, involved exposures of a bivalve, Mytilus edulis (Widdows et al., 1982). Of the hydrocarbons in the water-accommodated fraction (WAF), about 78% were monoaromatics; naphthalenes made up the majority of the remaining aromatics. The authors showed that food absorption efficiency and scope for growth were decreased and the labilization period for lysosomes decreased after exposure to 0.03 ppm hydrocarbons for 7 days. Energy balance was clearly reduced by about 35 days. The total exposure producing adverse effects was therefore between 0.2 and 1.0 ppm-days.

In recent flowing exposures to water extracts and chemical dispersions of Prudhoe Bay crude oil and distilled fractions of this oil, Anderson (1984, 1985) has determined the total exposure producing 50% mortality for fish and shrimp. The total exposure for 50% mortality for shrimp, Pandalus danae, was 0.05 ppm-days (total aromatics) during exposures to WSF extracts and chemical dispersions of fresh and weathered oil. This value is very consistent even with changes in the type of oil, the form of the oil (WSF or dispersion) and the duration of exposure (up to about 9 days). Sand lance (Ammodytes hexapterus) was more affected by oil droplets than soluble aromatics, while both contributed to mortality which generally was not observed until after 4 days. Significant latent mortality, 1 to 4 days following termination of exposure to 1-2 ppm indicated histological damage.

Physiological investigations with specific petroleum hydrocarbons or WSF and Alaskan marine species have recently been summarized by Rice et al. (1984). Table 15 (from their review) summarizes the concentration of test material required to produce the abnormal response as a percent of the 96-h LC_{50} value for each species. The response of pink salmon growth to WSF of Cook Inlet crude oil was quite sensitive (10% of LC_{50}), but most responses required an exposure of about one-third the 96-h LC_{50} concentration. The authors conclude that oil concentrations at 0.1 to 0.2 ppm total aromatics for 30 to 40 days could be harmful to the species listed in Table 15, particularly the invertebrates. This range of concentrations compares

Table 15. Sublethal effects of the water-soluble fraction (WSF) and individual components of crude oil on Alaskan marine organisms.

Species	Toxicant	Length of exposure (days)	Parameters affected	Percent of LC50 that affected parameters
Pink salmon (fry)[a,b]	WSF	40	Growth	30
	Naphthalene	40	Growth	28
	WSF	4	Opercular rhythm	20
Pink salmon[c] (alevins)	WSF	10	Growth	10
Coho salmon[d]	Toluene	40	Growth	50
	Naphthalene	40	Growth	32
Seastar (*Evasterias troschelii*)[e]	WSF	28	Feeding rate	28
	WSF	28	Growth	24
File periwinkle (*Thais lima*)[f] (now called *Nucella lima*)	WSF	28	Scope for growth	18
Blue mussels (adult)[g,h]	WSF	28	Scope for growth	19
		28	Byssal thread extrusion	15
Blue mussels[i]	WSF	40	Growth, development	61

[a] Moles and Rice 1983.
[b] Thomas and Rice 1979.
[c] Rice et al. 1975.
[d] Moles et al. 1981.
[e] O'Clair and Rice in press.
[f] Stickle et al. 1984.
[g] Stickle et al. in press.
[h] Babcock et al. in preparation.
[i] O'Clair and Rice in preparation.

closely with the range of 0.1 to 0.6 ppm total naphthalenes derived from sublethal studies on temperate species summarized in Table 14.

The use of behavioral measures to assess stress from environmental pollutants was reviewed by Olla et al. (1980). Many possible behavioral responses of marine species may be altered by environmental perturbations. The blue crab, Callinectes sapidus, was studied by Pearson and Olla (1979; 1980) and Pearson et al. (1981a). They found that this crab could detect naphthalene at 0.1 ng/l and that concentrations above 2 ppm (mg/l) produced defensive displaying and oriented locomotor activity. A WSF of Prudhoe Bay crude oil at 2 ng/l was detected by blue crabs and this concentration can be found in chronically polluted marine areas (Pearson et al., 1981a). As indicated by antennular behavior, a 24-h exposure to Prudhoe Bay crude oil (0.27 ppm) reduced the detection of chemical food cues by Dungeness crabs, Cancer magister (Pearson et al., 1981b). After 1 hour in clean water, the antennular response recovered indicating no structural damage to sensory cells.

Attempts to determine the threshold levels of petroleum exposure for marine species may be most productive when expressed in terms of the total exposure (days) to specific hydrocarbons (ppm of total aromatics). It appears that exposures to constant concentrations of oil extracts between 0.05 and 1.0 ppm-days (total aromatics) produce adverse sublethal responses in marine species.

TOXICITY OF HYDROCARBON-CONTAMINATED SEDIMENTS

Following a major oil spill or near a chronic point discharge of hydrocarbon-contaminated wastewater, hydrocarbons tend to accumulate in bottom sediments. The process by which hydrocarbons reach and are incorporated into sediments was discussed in detail in Section 3 of this review. Once incorporated into marine sediments, particularly in arctic climates, hydrocarbons may be quite persistent. Therefore it is not surprising that, following major oil spills, impacts have tended to be most persistent and recovery slowest in benthic sedimentary environments (see recent reviews by Teal and Howarth, 1984; and National Academy of Sciences, 1985). Much of our knowledge of the effects of oil-contaminated sediments on benthic populations and communities comes from opportunistic studies following oil spills. In many cases, an incomplete understanding of the structure and dynamics of the benthic communities prior to the spill has hampered interpretation of the magnitude and duration of adverse impacts from the spill. There have been relatively few carefully designed and executed laboratory studies of the effects of oil sediments on benthic marine organisms.

There are two important concerns with respect to impacts of oil contamination of marine sediments. The first relates to the toxicity of petroleum hydrocarbons associated with sediments and their long-term effects on benthic community structure and function. The second relates to contamination of benthic fauna and flora by hydrocarbons derived from contaminated sediments and possible transfer of these hydrocarbons through the marine food web to commercial fishery species (discussed in Section 5).

Effects on Individual Species

Several studies have shown a lack of significant mortality of benthic animals during exposures to concentrations of oil in sediments in excess of 1000 ppm (Wells and Sprague, 1976; Anderson et al., 1977; Roesijadi et al., 1977 and 1978). Krebs and Burns (1977) reported the mortality and adverse responses of the fiddler crab, Uca, living in sediment containing 1000 to 7000 ppm of petroleum hydrocarbons. Shaw et al. (1976) reported mortality of the clam, Macoma balthica, from sediment containing 640-3890 ppm (dry weight).

Several investigations have been performed of the sublethal responses of benthic marine invertebrates to oil-contaminated sediment or food (Percy, 1976; Shaw et al., 1976; Taylor and Karinen, 1977; Roesijadi and Anderson, 1979 and Augenfeld, 1980). The Arctic amphipod, Onisimus affinis, avoided oil-tainted food as well as oil masses, but the response diminished with preexposure to oil and with the use of weathered oil (Percy, 1976). Taylor and Karinen (1977) studied the behavior of the detritivore, Macoma balthica, in response to oil-contaminated substrate and oil extracts flowing over clean substrates. Since the clams burrow to the surface before dying (95%), they determined that 50% of those exposed three days to 0.37 ppm naphthalene equivalents surfaced, and 0.2 ppm inhibited burrowing within 60 min. Since a 1% (v/v) mixture of oil to seawater stirred for 20 h produces a naphthalene equivalent concentration of about 0.38 ppm, the above values are relatively high. Surface oiling of 670 mg oil/cm2 produced 50% surfacing by the clams in 24 h. No death was recorded in these four- to six-day experiments involving only a single oiling of the sediment. Shaw et al. (1976) produced significant mortality in the same species by applying fresh oil at doses of 5 mg of oil/cm2 daily for five days. Roesijadi and Anderson (1979) found that Macoma inquinata exhibited reduced survival, reduced condition index and reduced levels of free amino acids, particularly glycine, when exposed in the laboratory or field to sediments contaminated to about 1,200 mg oil per kg. Augenfeld et al. (1980) determined that the filter-feeding clam, Protothaca staminea, was more resistant to oiled substrates (about 1200 ppm) than Macoma inquinata (detritivore) as demonstrated by both higher survival and smaller alterations in free amino acid levels and condition index. Similar studies on the polychaete, Abarenicola pacifica, have shown that concentrations of 500 and 1000 ppm oil in sediment produced reduced feeding (measured by egestion rate) and decreased tissue glycogen concentrations (Augenfeld, 1980; Augenfeld et al., 1983). Clams (Protothaca staminea) less than 30 mm in size showed reduced growth after one year in sediments contaminated with oil (1,251 - 5,176 ppm). Greater effects were shown when the lower concentration of oil was mixed to depth (10 cm) in exposure trays (Anderson et al., 1983). Four- and six-month exposures of the same species to layers of sediment containing either oil or oil plus chemical dispersant (1:10) at about 2,000 to 3,000 ppm also reduced the rate of Protothaca staminea growth (Anderson et al., 1985).

In the NAS (1985) review a section was dedicated to the fate and effects of oil in polar environments. Table 16 contains the summary of

TABLE 16. SUMMARY OF EFFECTS OF OILED SEDIMENTS ON ALASKAN MARINE INVERTEBRATES

Species	Location	Sublethal Effect	Reference
Isopods			
Mesidotea entomon	Beaufort Sea	Inhibition of growth and molting only at high concentrations	Percy (1977)
M. entomon *M. sibirica*	Beaufort Sea	Neutral response to presence of oil, oil-tainted food, and contaminated sediments	Percy (1976, 1977)
M. entomon	Point Borrow	Readily recolonized contaminated sediment	Atlas et al. (1978)
Amphipods			
Boeckosimus affinis *Gammarus zaddachi*	Point Barrow	Food search success reduced, recovery occurs; no effect on respiration; reduced burrowing in contaminated sediments; reduced locomotory activity	Busdosh and Atlas (1977)
B. affinis *Gammarus oceanicus*	Beaufort Sea	Avoid oil, oil-tainted food, and contaminated sediments	Percy (1976)
Corophium clarencense	Beaufort Sea	Neutral behavior response to contaminated sediments	Percy (1977)
Pontoporeia femorata *Aceroides latipes* *Melita formosa* *Gammaracanthus loricatus* *Monoculodes* sp.	Point Barrow	Little or no recolonization of contaminated	Atlas et al. (1978)
Polychaetes			
Pectinaria hyperborea *Nephythys longosetosa* *Spio* sp.	Point Barrow	Attraction to oil-contaminated sediments	Atlas et al. (1978) Busdosh and Atlas (1977)
Acanthostephieia behrengiensis	Point Barrow	No recolonization of oil-contaminated sediments	Atlas et al. (1978); Busdosh and Atlas (1977)
Nereis vexillosa *Harmothoe imbricata*	Alaska	Sensitivity	Rice et al. (1979)
Mollusks			
Macoma balthica	Gulf of Alaska	Forced to surface when exposed to dissolved or sediment-absorbed oil	Taylor and Karinen (1977)

oiled sediment effects studies on Alaskan macroinvertebrates presented in the review. As pointed out above in the discussion on the toxicity of PAH in water, it is very difficult to compare the results of different studies on the basis of the ppm total aromatics producing an impact. Concentrations were not even included in the NAS review on polar studies. Without data quantifying concentrations of specific petroleum components in each exposure system, it is not possible to reach a conclusion on the relative sensitivities of infaunal species. In a study with the English sole, Parophrys vetulus conducted in Puget Sound McCain et al. (1978) carefully examined the change in petroleum hydrocarbon concentrations in the exposure sediments. They found an effect or the growth of the English sole and liver pathology resulting from exposure to sediments containing 700 ppm (dry weight) Prudhoe Bay crude oil. Aromatic hydrocarbons including trimethylbenzene and naphthalenes were found in the skin, muscle and liver of the fish at the first time interval (11 d). Later in the exposure (27 and 51 d) hydrocarbons were only found in the liver.

Several behavioral studies have been conducted with oil (Prudhoe Bay crude) contaminated sediments and bivalves or fish. Pearson et al. (1981b) showed that the crab, Cancer magister, consumed more littleneck clams (Protothaca staminea) from field enclosures containing oiled sediment (about 1,000 ppm) than from those with clean sand. They found in subsequent tests that clams in oiled sand exhibited more shallow burial and slower reburrowing than in control sand. Olla and Bjeda (1983) conducted a similar series of experiments with the hard clam (Mercenaria mercenaria) and also found oiling of sediments reduced the depth and rate of burrowing. The number of clams buried in 96 h was reduced, from control values, at 1,000 ppm with further reduction at 3,000 ppm.

Sand lance, Ammodytes hexapterus, is a prominent forage fish from California through Alaska and is known to bury in sand during the night and for long overwintering periods. Pearson et al. (1984) showed significantly decreased time spent buried in oiled (306 ppm) sand. Another experiment, oiled sand at 28 and 256 ppm did not reduce burial, but 3,384 ppm did. The lack of effect at 256 ppm corresponded to a higher condition index in the test group than that of fish used earlier (306 ppm). There was an apparent interaction between the use of a contaminated refuge and the nutritional state of the fish. Interaction between oil contamination and sediment grain size preference for A. hexapterus was studied by Pinto et al. (1984). Sand lance avoided gravel and silt and preferred to bury in fine or coarse sands. The fish preferred clean gravel when sand was oiled at about 120 or 1,000 ppm. If only silt and oiled sand are provided as choices, sand lance prefered to remain in the water column.

BIOLOGICAL EFFECTS OF OIL SPILLS AND CHRONIC LOW-LEVEL DISCHARGES OF HYDROCARBONS

A vast number of scientific papers has been published and technical reports produced dealing with the biological impacts of the oil spills summarized in Table 4. Results of many of these investigations have been summarized in reviews by Clark and Finley (1977) and Teal and Howarth (1984), and NAS (1985).

Massive kills of shallow and intertidal benthic organisms occurred whenever and wherever large amounts of fresh crude or refined oil came ashore. Massive immediate kills either did not occur or were impossible to document in spills and blowouts that occurred well offshore and resulted in little or no stranding of fresh oil (*Argo Merchant*, *Chevron*, *Ekofisk*, *IXTOC I*). In the *Florida* diesel fuel spill, massive kills occurred in heavily oiled sites where sediment hydrocarbon concentrations exceeded about 130 ppm. Following the *Amoco Cadiz* spill, there were massive reductions of some species, such as ampeliscid amphipods, where sediment hydrocarbon concentrations exceeded 50-100 ppm. Ampeliscid amphipod populations also were severely damaged in the *Florida* and *Tsesis* spills. These amphipods apparently are among the most sensitive dominant benthic species in many temperate and subarctic marine environments.

Littoral macroalgae appear in most cases to be fairly tolerant of oiling, though as in the *Torrey Canyon* spill, they may be smothered by massive deposits of oil. In some cases, a sensitive species (e.g. *Ascophyllum*) was eliminated and was replaced rapidly by a more tolerant species (e.g. *Fucus*). In most cases, the macrofauna associated with the macroalgae was decimated wherever significant amounts of oil came ashore. In the case of the *Torrey Canyon* spill, much of the damage to the rocky intertidal fauna was attributed to use of large amounts of chemical dispersents containing aromatic solvents to clean the shore.

Intertidal salt marshes, particularly those containing peaty high-organic soils, tend to be quite sensitive to oil spills, particularly if the oil is fresh when it reaches the marsh and the marsh grasses are in the active growth phase. Coastal marshes of Buzzards Bay, Massachusetts, impacted by diesel fuel from the *Florida* spill were severely damaged and recovery was incomplete even eight to twelve years after the spill (Sanders et al., 1980). Several marshes, especially that at Ile Grande, were severely impacted by the *Amoco Cadiz* spill, but were subsequently destroyed during the cleanup operation. Following the *Arrow* spill, Nova Scotia marshes damaged by the Bunker C residual oil experienced a die-off of *Spartina alterniflora* one year after the spill, with substantial recovery observed two years later.

Damage to commerically important shellfish has been variable. There were large losses of intertidal clams *Mya arenaria* following the *Florida* and *Arrow* spills of refined oil products. Following the *Amoco Cadiz* spill, oysters, shrimp and lobsters became heavily contaminated with oil, but did not experience high mortalities. In fact, numbers of commerical shrimp actually increased along the north coast of Brittany in the two years following the *Amoco Cadiz* spill, possibly due to decreased predation or increased microbial and algal production. Abundance of some microfaunal and meiofaunal species may increase in moderately oiled sediments, providing increased food for benthic deposit-feeders such as the clam *Macoma* and the polychaete *Arenicola*.

Very few impacts, other than tainting, have been observed in phytoplankton and zooplankton communities following oil spills. Following the *Tsesis* spill in the Baltic Sea, phytoplankton and planktonic bacterial biomass increased, possibly due to a decrease in the abundance or feeding activity of the larger zooplankton. Some evidence of contamination and sublethal stress in zooplankton populations was reported following the *Arrow*, *Argo Merchant* and *Amoco Cadiz* spills. These impacts apparently were of short duration and areal extent.

Adverse impacts on commercially important pelagic and demersal fish were reported following the *Argo Merchant*, *Tsesis* and *Amoco Cadiz* spills. A year after the *Tsesis* spill, spawning frequency and hatching success of herring *Clupea harengus* were reduced. For up to three years after the *Amoco Cadiz* spill, plaice *Pleuronectes platessa*, collected from oil-contaminated estuaries exhibited a variety of biochemical changes and histopathological lesions. In female plaice from the contaminated estuaries, there was evidence of delayed or suppressed ovarian development. Growth rate and fecundity of the fish were reduced.

The long-term environmental impacts of chronic low-level point-source effluents containing PAH are quite different from those of massive oil spills. There usually is no massive die-off of marine fauna and flora. Instead, there may be a gradient of impact, characterized by altered community structure, abundance, and diversity extending around the pollutant source. There have been several investigations of impacts of refinery effluents and oil tanker terminals on the coastal marine environment (see review of Dicks and Hartley, 1982) and a few studies of impacts of produced water discharges (see review of Neff, 1985).

As discussed above, approximately 150 metric tons per year of petroleum hydrocarbons, including about 4 tons of low molecular weight PAH, are discharged from the ballast water treatment facility to Valdez Harbor. The mean water depth of Valdez Harbor is 180 meters and the water is highly stratified, particularly during the summer. The effluent diffuser system discharges treated ballast water below the density discontinuity and there is little evidence of vertical mixing of discharged hydrocarbons into the surface waters (Lysyj et al., 1981). Maximum hydrocarbon concentrations occur at about 50 meters water depth in spring and summer. Three to five meter tides afford fairly rapid exchange of water in the harbor and probably provide the major mechanism for elimination of hydrocarbons from the harbor. Because the discharged hydrocarbons remain deep where temperatures rarely rise above 5°C, photodegradation, evaporation, and microbial degradation probably play only minor roles in removal of PAH from the harbor. PAH not flushed from the estuary probably accumulate in bottom sediments where they may persist indefinitely.

It appears then that the benthos is where biological impacts of the discharge are most likely to occur and where they should be sought. Cowell and Monk (1981) proposed monitoring of intertidal rocky shore populations. To date, results of several pre-discharge baseline studies and some preliminary post-discharge studies have been published on the benthos of Valdez Harbor (Feder and Matheke, 1980). Diversity of benthic fauna is low in deeper parts of the harbor because of low dissolved oxygen, and significant impacts of the ballast discharge have not been documented.

Milford Haven on the west coast of Great Britain has a physiography somewhat similar to that of Valdez Harbor and has been the site of a major oil port and refinery complex since 1960. Extensive environmental studies at Milford Haven extending over the last two decades have been summarized by Dicks and Hartley (1982). It has been estimated that approximately 238 metric tons (270,000 liters) of petroleum hydrocarbons enter Milford Haven each year from all sources. This is nearly twice the amount being discharged each year from the ballast water treatment plant into Valdez Harbor. There have been changes in community structure of intertidal and benthic fauna and flora in some parts of Milford Haven attributable to the hydrocarbon inputs. However, there has been no general decline in the marine flora and fauna. The lack of more substantial impacts was attributed in part to rapid flushing of the estuary.

Reported impacts of effluents from oil refineries have been quite variable. Impacts of a refinery effluent to Littlewick Bay in Milford Haven were restricted to an area of about 200 meters around the outfall. However a refinery effluent to the Medway estuary on the east coast of Great Britain caused substantial damage to intertidal macrofauna extending out to at least 1.5 km from the outfall (Warfe, 1975). Discharge of refinery effluent to a salt marsh environment on the south coast of Great Britain caused substantial damage to the salt marsh vegetation (Dicks and Hartley, 1982). Subtidal benthic communities also were damaged. Only two benthic polychaete species survived near the outfall. Effluent quality (hydrocarbon concentration) was improved and volume decreased between 1972-1974. This resulted in a gradual recovery of the salt marsh vegetation. After about ten years, the marsh appeared healthy, though species composition of plants and animals still was different from that in nearby uncontaminated areas. Subtidally, there was little evidence of recovery.

The environmental impacts of the produced water discharges to Cook Inlet probably are minimal despite their large volume, because of the dynamic nature and rapid flushing of the water in the inlet. However, no detailed long-term studies have been performed to date.

The best investigations of the impacts of produced water and related production discharges from oil platforms are those in Trinity Bay, Texas and the Forties Field in the North Sea.

Trinity Bay Texas is a shallow, low-salinity estuary, very much unlike Cook Inlet. However, it does in some ways resemble some nearshore environments of the Alaskan Beaufort Sea where produced water might be discharged in the future. During the 20-month timecourse of the Trinity Bay study, produced water with a mean total hydrocarbon concentration of 15 ppm was discharged from the separator platform through an outfall one meter above the bottom at a rate of 650,000 to 1,590,000 liters/day (Armstrong et al., 1979). Hydrocarbons were diluted nearly 2,500-fold in the water column within 15 meters of the outfall. Bottom sediments were heavily contaminated with medium molecular weight alkanes (C_{10}-C_{28} n-paraffins) and aromatics (C_3 benzenes - trimethylphenanthrenes).

There was a gradient of decreasing naphthalenes concentrations from a mean of about 21 ppm 15 m from the outfall to background 500 to 4800 m from the outfall, depending on direction. There was an inverse gradient of numbers of organisms and numbers of species of benthic infauna with distance from the outfall. Within 15 m of the outfall, the bottom was almost devoid of organisms. Benthic faunal abundance was significantly reduced out to approximately 150 m in all directions from the outfall. At stations located 685-1675 meters from the outfall, there was an apparent enhancement of the benthic fauna, with greater numbers of individuals and species at these stations than at reference stations 4,000-5,800 m from the outfall. Thus, a 150-m radius zone of adverse impact was observed, with an apparent zone of enhanced faunal abundance and diversity further out from the discharge, and impacts were correlated to comtamination of sediments with petroleum hydrocarbons. Armstrong et al., (1979) estimated that a nominal concentration greater than about 2 ppm total naphthalenes was necessary to significantly reduce benthic infaunal populations of Trinity Bay. Results of these investigations should be extrapolated to offshore situations with extreme caution. The shallow turbid nature of the receiving water is unlike the situation encountered offshore, with the possible exception of some near shore areas of the Beaufort Sea. Where water depth is greater and suspended sediment concentrations are lower than those encountered in Trinity Bay, a much smaller fraction of the hydrocarbons in the discharged produced water will be deposited in bottom sediments near the outfall, and adverse effects on the benthos will be much less severe.

Hartley and Ferbrache (1983) recently reported the results of a similar benthic monitoring study in the Forties Field located in the British sector of the North Sea in 100-125 meters of water approximately 177 km northeast of Aberdeen, Scotland. The 80 wells drilled to date from four platforms were drilled with water base muds. Current rate of produced water discharge was not stated. It is expected to increase with the age of the field and oil-water separators were built on each platform with a nominal capacity of 40 million liters per day.

Production from the field began in September, 1975, and three benthic surveys have been performed to date; in June, 1975, before production began, and in 1978 and 1981. Concentrations of aliphatic hydrocarbons in sediments measured by gravimetric techniques have shown a slight rising trend from a mean of 5.7 ppm in 1978 to 8.9 ppm in 1981. Grain-size distribution of sediments did not change significantly at any sampling stations during the three surveys. No analyses were performed on metals in sediments.

The benthic fauna was rich and diverse throughout the study area. However, directly beneath the Platform C and to about 100 meters to the west, the benthic macrofauna were severely depressed and there was evidence of hydrocarbon contamination (305-470 aliphatics), possibly from diesel fuel. The abundance of the polychaete Chaetozone setosa was much higher near Platforms A and D than at other stations. Abundance of another opportunistic polychaete, the capitellid Capitomastus minimus, increased in muddier sediments to the west of the rigs between 1978 and 1981. Rate of uptake and mineralization of $_{14}$C-naphthalene by sediment microbiota increased with decreasing distance from platforms in the Forties Field (Saltzmann, 1982). In addition, three species of demersal fish (cod, whiting and haddock) had slightly elevated activity of hepatic aryl-hydrocarbon hydroxylase (aromatic hydrocarbon detoxification enzyme system) compared to the same species collected in a reference area about 30 km west of the field. Overall, it is apparent that impacts of oil production activities from the Forties oil field have been localized (primarily within 450 m of the platforms) and of low magnitude.

There is little doubt that a massive oil spill in the near shore Alaskan marine environment (i.e. from the grounding of a large tanker leaving Valdez or Cook Inlet) would cause serious damage to important components of the marine ecosystem, as occurred following the Amoco Cadiz spill. Low ambient water temperatures are likely to decrease the rate of evaporation, photooxidation and biodegradation of spilled oil increasing the residence time and potential environmental damage of the more toxic, low molecular weight PAH. Available evidence would seem to indicate that current discharges of produced water to Cook Inlet and treated ballast water to Valdez Harbor are not causing significant environmental damage. However, seasonally low water temperatures and incident light intensity slow the rate of degradation of PAH, possibly allowing for their gradual accumulation over several years in bottom sediments. Efforts should be made to monitor long-term trends in concentrations of PAH in sediments and associated biota in the vicinity of these chronic discharges to determine if serious long-term biological impacts might occur.

RECOVERY OF BENTHIC COMMUNITIES

In the previous section of this chapter we reviewed the biological effects of oil spills and chronic effluents. Most of the study results dealt with the impacts of spills on benthic comunities. Therefore, this section will summarize findings related to the recovery of benthic communities from either accidental or experimental contamination with oil.

Following a spill of No. 2 Fuel oil in Buzzards Bay off West Falmouth, Massachusetts in September, 1969, extensive long-term investigations were performed on the process of recovery in the spill-impacted salt marsh and shallow benthic environment (Sanders, 1980; Sanders et al., 1980). At the most heavily impacted benthic station studied in Wild Harbor, hydrocarbon concentrations in sediments were quite variable, reflecting a patchy distribution. However, concentrations remained above 1,000 ppm, and as high as 12,400 ppm between October, 1969 and September, 1971. There was an immediate near-total eradication of the benthic fauna at this station. This was followed within three months by a rapid increase in the abundance of the opportunistic polychaete Capitella capitata, which reached densities of up to 95,000 per m^2 by May, 1970. After about seven months, Capitella populations crashed and were replaced by a few less opportunistic species. Number of individuals and species abundances fluctuated widely, and by the end of two to three years had not risen to levels encountered there at the time of the spill.

At stations just offshore from Wild Harbor, petroleum hydrocarbon contamination of sediments following the spill was much less severe than in the harbor. At Stations 9 and 10, sediment total petroleum hydrocarbon concentrations were in the range of 150 to 250 ppm in October to November, 1969, and had dropped to the range of 46 to 88 ppm by mid to late 1971. At these stations, number of species and faunal densities dropped to low levels during the seven to eight months after the spill. In July to August, 1970, densities and numbers of species rose greatly. This resulted from recruitment of larvae from the water column and resulted in a 20- to 30-fold increase in number of species. The benthic fuana at this time were dominated by the opportunistic capitellid, Mediomastus ambiseta. This was followed in late 1970 by a sharp decline in density and species abundances which continued to fluctuate seasonally at lower levels during 1971 and 1972. Sanders (1978) interpreted the higher species abundance and lower faunal density and variation during the third year after the spill to be indicative of some recovery.

Sediments at slightly oiled stations further offshore never contained petroleum hydrocarbons at concentrations higher than about 50 to 80 ppm. These stations showed little variation in species composition and much smaller variations in density than inshore stations during the three-year post-spill investigation. Thus, it would appear that sediment hydrocarbon concentrations from No. 2 Fuel oil below about 100 ppm allow early recovery to proceed, and concentrations in the range of 50 to 80 or less do not seriously affect benthic communities.

Investigations have indicated that meiofaunal communities, particularly of estuarine areas, are quite resilient following natural disturbance or organic pollution (i.e., Cato et al., 1980). For example, Alongi et al. (1983) studied recolonization of meiobenthos in trays containing azoic sandy sediments with or without added crude oil (Prudhoe Bay crude oil). The trays were deployed in 1 m of water in the lower York River, Virginia during the summer. Total petroleum hydrocarbon concentrations in the the sediments in the trays initially ranged from 47 to 9,100 ppm, with total aromatic hydrocarbons initially ranging from 0.43 to 136 ppm. The rate of recovery of the different meiofaunal groups was very rapid in surficial sediments and somewhat slower in deeper sediments, below the redox potential discontinuity, in the trays. Nematodes were the dominant meiofaunal taxon in all treatments, and also were the slowest to recover in the trays to abundance and community composition similar to that in study site control sediments. In fact, recovery of nematodes was not complete in 90 days in deep sediments in the middle and highest oiled trays. The results of this study indicate that recovery of benthic meiofauna was complete at 28 days at all depths in sediments containing 3,900 ppm total oil and 29 ppm aromatic hydrocarbons initially and 1,285 ppm total oil in 15.75 ppm aromatic hydrocarbons at 28 days.

Similarly, Boucher (1980) reported little change in the abundance of meiofaunal nematodes and harpacticoid copepods in subtidal fine sand sediments in 19 m of water in the Bay of Morlaix, France, heavily impacted by the Amoco Cadiz oil spill (up to 3,800 ppm saturated petroleum hydrocarbons in sediments). However, there was evidence of a decrease in nematode diversity in the oiled sediment, due to an increase in the abundance of a few dominant species following the spill.

Two small estuaries on the north coast of Brittany, France, Aber Benoit and Aber Wrac'h, became heavily contaminated with Amoco Cadiz oil following the spill. Glemarec and Hussenot (1982a, b) investigated the recovery of the benthic macrofauna of the two estuaries following the spill. The estuaries contain a wide variety of different soft substrates, from fine intertidal muds to coarse sand flats, so it was possible to study the course of recovery of different types of sediment regimes.

During the three months after the spill, oil spread throughout the estuaries, and sediment petroleum hydrocarbon concentrations in most areas were in the 1,000- to 10,000-ppm range (measured by infrared analysis: Marchand et al., 1981). The exceptions were the coarse sandy areas at the mouths of the estuaries. There were immediate massive kills of the benthic fauna of the estuaries after the spill, and nearly all communities still were extremely depauperate eight months later. The coarse sand communities at the mouth of Aber Wrac'h were little affected by the spill and showed near normal seasonal fluctuations. The highest oil concentration measured in these coarse sand sediments was 1,020 ppm in May, 1978, three months after the spill. In the subtidal dune-sand sediments off Aber Benoit, petroleum hydrocarbon concentrations never exceeded 50 ppm, and there was some evidence of only a temporary decrease in total abundance with no significant change in benthic community structure.

Muddy sediments at the heads of the estuaries were the most heavily oiled and most severely damaged. After eight months, highly opportunistic species, characteristic of early stages of recovery from organic pollution, began to appear and reached very high densities. Peak abundance of opportunists was not reached until 20 to 25 months after the spill. At most other locations in the estuaries, characterized by fine sands and muddy sands, dominant benthic fauna eight months post-spill included the less extreme opportunist species, primarily cirratulid and capitellid polychaetes (e.g., Chaetozone setosa, Heterocirrus spp., Polydora spp., Cirratulus cirratulus, etc.). After about 17 months, these opportunists were joined by a group of sensitive species which typically disappear following a perturbation and then reappear over a broader ecological range (e.g., Spio sp., Notomastus laetericeus, Phyllodoce spp., Nereis diversicolor, etc.).

Winter storms resulted in sediment resuspension and a decrease in some cases in sediment hydrocarbon concentrations. These were followed, especially in the second winter after the spill, by a decrease in opportunists and an increase in later successional stages. In Aber Benoit, the decline in opportunistic species, and replacement by later successional stages began after eight months in well-oxygenated dune sands, after 13 months in heterogeneous muddy sands, after 17 months in fine sands and sandy muds and after 25 months in the muddy sand areas at the head of the estuary. Two to two and a half years after the oil spill, the communities of the dune sand areas had recovered completely, while earlier successional stages still were evident at all other substrates. Communities in Aber Wrac'h recovered more slowly than communities in similar substrates in Aber

Benoit. Glemarec and Hussenot (1982a, b) estimated that it would require three to four years for benthic communities of the Abers to return to normal or to a new equilibrium condition.

Cabioch et al. (1982) and Dauvin (1982) reported similar changes following the Amoco Cadiz oil spill in benthic communities occupying different sediment types in deeper coastal waters of the Bay of Morlaix. Coarse sandy sediments were little affected by the spill and their communities recovered rapidly. The fauna of fine muddy sand, particularly several species of amphipods of the genus Ampelisca, were severely impacted by the hydrocarbons and were very slow to recover. Significant recolonization of severely impacted sediments did not begin until the second annual cycle of recruitment (spring, 1980). There was further substantial recruitment in the third spring following the spill. The dominant fauna of the heavily impacted offshore fine sand sediments during the next year after the spill were opportunistic species of capitellid and cirratulid polychaetes. Approximately three years after the spill, the communities of the fine sandy sediments in the Bay of Morlaix had returned to the normal pre-spill range in terms of density, species richness, and biomass. Abundance of amphipods still was depressed in some areas.

Following the grounding of the Soviet tanker Tsesis on the Swedish coast of the brackish Baltic Sea south of Stockholm in October, 1977, approximately 1,000 tons of medium grade (No. 5) Fuel oil were released (Elmgren et al., 1983). Although about two-thirds of the oil was recovered mechanically, significant amounts of oil reached the rocky shores and the benthic environment.

Within 16 days after the spill, an estimated 95 percent of the dominant amphipods, Pontoporeia affinis and P. femorata and polychaetes, Harmothoe sarsi were eliminated from the benthos at the most severely impacted station. The deposit-feeding clam (Macoma balthica) was resistant to the pollution but became heavily contaminated with oil (up to 1,000 ppm dry wt.). All meiofaunal groups except nematodes were reduced in abundance in the affected area.

In the summer following the spill (1973), there was a very heavy recruitment of juvenile Macoma balthica in areas where amphipods had been virtually eliminated. Not until the summer of 1979 did amphipods, Harmothoe sarsi, and harpacticoid copepods begin to return to sediments of the most heavily impacted stations, and oil contamination of Macoma balthica decrease to 1,000 ppm. By the third year after the spill, abundance of amphipods still was depressed but Harmothoe sarsi had returned to its pre-spill abundance. Oil concentrations in Macoma balthica had dropped to about 250 ppm. Because of the long life span of Macoma balthica, the authors predicted that the disturbed community structure at the heavily oiled stations would persist for several years. Full recovery could take five to ten years.

Leppakoski and Lindstrom (1978) studied recovery of benthic macrofauna in a small low salinity (5.4-6.7°/₀₀ salinity) harbor on the Finish coast of the Baltic Sea receiving effluents from an oil refinery, following nearly complete abatement of the oily waste discharges. The toxicity of sediments to benthic insect (Chironomus plumosus) larvae decreased markedly in the first three years following cessation of oily wastewater discharges. Number of species and individuals, and species diversity of benthic macrofauna increased sharply at stations near the former outfalls. However, three years after abatement, there was a trend toward reduced diversity, characterized by a marked increase in the dominance of the bivalve Macoma balthica, as occurred following the Tsesis oil spill. Thus, substantial but not complete recovery of the benthic community had occurred three years after near complete cessation of oily wastewater discharges to the harbor.

Vanderhorst et al. (1978, 1979, 1980 and 1981) utilized trays of sediment with mesh bottoms placed in the field (intertidal and subtidal) to measure recruitment of infaunal species and loss of petroleum contamination. Using this approach it was possible to predetermine the number of replicate trays and cores from these trays required to detect a 50% reduction in the numbers of individuals and species with 95% confidence (Vanderhorst et al., 1978). Vanderhorst et al. (1981) experimentally evaluated the effect of oil treatment, site, substrate type, season and tide level on the composition, density and species richness of organisms colonizing substrates which were initially free of organisms. Significant differences for some biological parameters were demonstrated for each of the types of treatment contrast (site, substrate type, season, tide level, and oil). Significant biological effects were demonstrated to be due to oil treatments for 70% of 56 biological parameters evaluated in detail.

Predicted full recovery for sand habitats in Puget Sound was 31 months following an initial oil treatment of 1,800 ppm. Predicted full recovery for a commercial clam bed habitat was 46 months following an initial oil treatment of 2,500 ppm. The studies of Vanderhorst et al. (reviewed in Vanderhorst, 1984) used sediments devoid of benthos as a starting substrate. All infauna identified and counted in the trays had to either migrate from surrounding substrates or settle as larvae. In an actual spill some organisms may well survive, thus increasing the rate of recovery of the total benthic community.

SUMMARY

Virtually all the investigations to date of the recovery of benthic communities from acute or chronic pollutant stress have been performed in estuarine and nearshore coastal waters. Under these conditions, the responses to and recovery from petroleum hydrocarbon pollution have been remarkably similar.

Factors which did seem to affect the rate of recovery include: water depth, to the extent that it influenced the amount of storm-induced sediment resuspension; magnitude of pollutant accumulation in the sediments; sediment grain size (recovery was more rapid in coarse than in fine sediments); and availability of planktonic larvae for recruitment.

Fuel oils (No. 2 and No. 5 Fuel oils) seem to produce more severe impacts and result in slower recovery than crude oil. This undoubtedly is due to the higher concentration in fuel oils than in most crude oils of light aromatic hydrocarbons, particularly the toxic naphthalenes and phenanthrenes (Neff and Anderson, 1981).

Generally, the estuarine and coastal marine benthic ecosystems studied to date recovered rapidly from petroleum pollution. Recovery times of a month (meiofauna) to five to ten years have been suggested. This rate of recovery lends support to the conceptual model of Boesch and Rosenberg (1981) that estuarine communities are more resistant to stress than strictly marine communities because they are composed of more eurytolerant species. In addition, such communities are more resilient than oceanic communities because they include more opportunistic species acclimated to frequent disturbance.

ALASKAN PERSPECTIVE

Alaskan marine animals do not appear to be significantly more sensitive to aromatic hydrocarbons than similar species from more temperate and tropical climates. however, because the volatile, toxic light aromatic hydrocarbons associated with spilled oil tend to persist longer in the water column at low water temperatures characteristic of Alaskan waters than at higher water temperatures, biological impacts of oil spills in Alaskan waters may be more severe than those in warmer climates. The greater persistence of spilled oil in arctic marine sediments and shorelines, compared to more temperature climates, may result in a substantially slower recovery of damaged marine ecosystems. However, many Alaskan benthic and coastal environments already are severely stressed by natural environmental extremes such as seasonal ice cover or scouer, freshwater runoff, and high suspended sediment loads. The biological communities inhabiting such environments are dominated by large populations of rapidly reproducing opportunistic species, the very species that are the first to return to a site damaged by oil or other organic pollution. Such marginal, naturally stressed communities tend to recover rapidly from acute pollution events such as oil spills.

Under such circumstances, the populations most likely to be severely impacted by and exhibit the slowest recovery from an oil spill are the large long-lived species such as king crabs, salmon, and marine mammals. With few exceptions, early life stages of these large animals are much more sensitive to oil and other toxicants than later life stages. Thus, the most severe damage to the Alaskan marine environment from an oil spill would result from destruction of the early life stages of these large species or damage to their preferred habitats.

7. INFORMATION NEEDS AND RECOMMENDED MONITORING STRATEGIES

The Alaskan marine environment is so vast and varied that, despite the tremendous advances made during the last ten years due in large part to the NOAA-OCSEAP Program, our knowledge of the physical, chemical, and biological processes by which the Alaskan marine environment functions is still very fragmentary. The more we know about the natural processes that control a marine ecosystem, the easier it is to design a meaningful monitoring program to detect the long-term impacts, or lack thereof, of man's activities. However, neither time nor financial resources will allow us to learn everything about the Alaskan marine environment. Therefore, in the present context, it is necessary to focus on better understanding those processes which we expect to have the greatest influence on the fate and effects of PAH and related hydrocarbons in the Alaskan marine environment.

INFORMATION NEEDS

Based on the information discussed in this review, we have identified several data gaps or information needs and have developed some general strategies for design of long-term monitoring programs.

1. More information is needed on the sources, both natural and anthropogenic of PAH and related hydrocarbons in the Alaskan marine environment. A more complete and quantitative inventory should be developed of PAH discharged from major known point sources: i.e., treated produced water and ballast water discharges, natural oil seeps, domestic and industrial sewage, oil-contaminated drilling fluids, onshore oil handling and trans-shipment facilities and other industrial activities. Non-point sources should be better characterized: i.e., vehicular exhaust, including boats; open burning and fores fires; home heating, particularly with wood and coal; erosion of peat coal and other PAH-containing strata; arctic haze; etc. With such an inventory, it will be possible to predict better the consequences of potential new inputs of PAH from accidental (i.e., oil spills) and intentional (i.e., allowing discharge of produced water to the Beaufort and Bering Seas) new sources.

2. Our knowledge of the hydrocarbon composition of produced waters from different sources is very incomplete. It is possible, even likely, that the composition of produced water will change with time over the life of a well, or be different from one well to another in a given area. Yet the published

information on the composition of produced water from offshore wells comes from a few spot analyses of produced water from Cook Inlet, the Gulf of Mexico and southern California. Most analyses have been of the light hydrocarbon fractions only (low molecular weight alkanes and monoaromatics). There are very few analyses of medium and high molecular weight PAH In produced water, and virtually none of the non-hydrocarbon organic fractions which may constitute more than 90 percent of the dissolved organics in produced waters. A long-term research program to characterize the organic composition of produced waters discharged to the Alaskan marine environment would be very valuable. Samples of produced water could be taken once or twice a year for several years from all produced water discharges to Alaskan marine waters. The samples should be analyzed by the latest methods for individual alkanes and aromatics, through C_{34} and benzo(a)pyrene, respectively, for sulfur and nitrogen heterocyclics, triterpenes and steranes, and for organic acids and phenols.

3. The environmental fate and effects of treated produced water and ballast water discharges to Alaskan coastal waters should be studied in more detail. What is the residence time (half-life) of ballast water hydrocarbons in Valdez Harbor? Are there any sinks for these materials in the harbor where they may accumulate to high concentrations over time? What biota are most likely to come in contact with and be affected by these chronic discharges? The same questions can be asked about produced water discharges to Cook Inlet.

4. The focus of much new oil exploration and development offshore Alaska in the next several years will be in the Beaufort Sea and northern Bering and Chukchi Seas. Our knowledge of the biological processes in these arctic seas is very poor. In many cases, we have very incomplete knowledge of such basic processes as the structure of the marine food webs leading to commercially important or inherently valued marine species (i.e., arctic cisco, marine mammals). In addition, we know very little about the sensitivity of these truly arctic species to oil and hydrocarbons. Most work on the toxicity of petroleum hydrocarbons to Alaskan species has been performed at the NOAA laboratories in Seattle, Washington, and Auke Bay, Alaska, with subarctic species. Are arctic species more or less sensitive than subarctic species to petroleum hydrocarbons? What is the timecourse and magnitude of induction of the mixed function oxygenase system in arctic fish? Can arctic invertebrates metabolize PAH? What is the timecourse and extent of bioaccumulation and depuration of PAH by arctic marine animals?

5. There have been extensive efforts for the past several years to model the behavior and fate of spilled oil under arctic sea-ice conditions. These models should be field-verified and tested in carefully designed experimental spills in the field. The models and field data should be used to develop optimal strategies for treating or counteracting spills under different environmental and climatic conditions.

MONITORING PROGRAMS

1. A long-term monitoring program should be initiated to assess the fate and effects of produced water discharges to Cook Inlet. This monitoring program should include characterization over time of the volume and chemical composition of produced water discharged from an offshore platform or shore-based treatment facility; modeling or actual tracking of the movements and dilution of the produced water plume in the water column; deposition and accumulation of hydrocarbons and metals from the produced water discharge in bottom sediments near the discharge or at possible depositional sites, if any, in the vicinity.

   Until reliable remote water sampling devices are developed for taking integrated samples over weeks, bivalves are likely the best means of obtaining an integrated sample of bioavailable (potentially toxic) contaminants. When a sediment trap is deployed above the cage of bivalves at various stations around a discharge, there is the opportunity to compare particulate-bound contaminants with those bioaccumulated. In the benthic environment, detritivorous bivalves, such as _Macoma_ species, have been shown to bioaccumulate contaminants from sediments. Containers (trays, cages in the bottom, etc.) with these clams can be placed on the bottom at different distances from the outfall. In addition to determining bioaccumulation, the condition index, growth, and energy balance (scope for growth) can be measured on these bivalves.

   It is necessary to determine the impacts on the infaunal community (balanced indigenous population, BIP). Based on previous studies, the strongest statistical evidence for impacts to benthic populations has come from experimental installations of substrate to determine effects on recruitment. Reciprocal transplants of sediment trays will provide evidence of impacts from the water and sediment separately.

   With proper planning it is possible to design experimental installations at various distances from the discharge that will determine:

a. accumulation of contaminants at the surface microlayer, in the water column, and on the bottom;

b. relation between the bioaccumulation of toxic components and the degree of impact on organisms;

c. spacial extent of impacts on individual species and the benthic recruitment of larval stages of many species.

It would appear that these findings would answer all the key questions posed by the resource manager attempting to protect the marine environment of Cook Inlet, Alaska.

2. Offshore development and production of oil reservoirs is just getting underway in the Beaufort and could well start in several parts of the Bering Sea in the next decade. A long-term effects program should be performed during development of new offshore oil fields in these frontier areas.

   At an early stage in the design of this program, a clear definition should be developed of what constitutes a significant environmental impact. Particular attention should be paid to defining impacts that, if they occurred, would be of consequence relative to commercially important or intrinsically valued resources of the area. The monitoring program should be designed specifically to identify these impacts. Most major environmental monitoring programs in the past have suffered severely or even failed due to a lack of clear definition of what constitutes an undesirable impact.

   If the major objective of the monitoring program is to document long-term trends in the magnitude and areal extent of environmental change attributable to the development activity, a fairly modest program may be adequate. A carefully-selected set of physical, chemical, and biological samples and measurements could be taken on an annual basis at a relatively small number of stations along a potential pollution gradient in the development field. The nearest stations would be within 200 m of the development platform in order to maximize the likelihood of detecting a "signal." Observations would be made and samples taken at the same time each year for at least the duration of development of the field. Such a design is particularly appropriate for the Beaufort and northern Bering Seas, because field sampling is extremely difficult for all but a brief open water period each year (mid-August to mid-September). Selection of parameters to measure should be based upon the definitions of impact as described above and might include characterization of rates and long-term trends of change in benthic community structure, recruitment and age-size structure; induction of mixed function oxygenase activity in demersal fish from the area; and measures of reproductive success, fecundity, and growth in representative indigenous populations, possibly including sentinal organisms (i.e., the mussel watch concept). An essential component in such a monitoring program is to correlate long-term trends in biological parameters with trends of change in concentrations of contaminants in sediments and biota. Contaminants of concern include aromatic hydrocarbons and heavy metals.

8. SUMMARY

The major point sources of polycyclic aromatic hydrocarbons (PAH) in the Alaskan marine environment are discharges of treated produced water, crude oil tanker ballast water and domestic/industrial sewage. These, as well as new point sources of PAH, can be expected to increase in number and volume as offshore reserves of oil and gas are developed and industrial activity in Alaska increases. Currently, these point sources contribute only a small portion of the total PAH entering the Alaskan coastal waters from all sources. Major non-point sources of PAH in Alaskan coastal waters and sediments are aerial deposition of particle-bound PAH derived from remote industrial and other combustion sources. Burning of wood for home heating and in controlled or wild forest fires may be major sources of these airborne particulate PAH in some parts of Alaska. Additional important sources of PAH include erosion of peat and coal deposits and submarine oil seeps.

The composition of hydrocarbon assemblages in marine sediments of developed and remote areas of Alaska reveal a predominantly biogenic (natural) and pyrogenic (combustion) origin. Oil spilled in the ocean under arctic and subarctic conditions similar to those in Alaska tends to be quite persistent. In coastal areas characterized by high suspended sediment loads, such as Cook Inlet, the Beaufort Sea and Norton Sound off the Yukon River, PAH from spilled oil will adsorb rapidly to suspended sediment and be transported to the bottom, where they will be quite persistent. Evaporation of low molecular weight aromatic hydrocarbons is slow at low water temperatures and is nearly completely impeded by ice cover.

The main mechanisms of removal of PAH and related hydrocarbons from Alaskan marine waters are evaporation, photochemical and chemical degradation, and metabolism by marine bacteria, fungi, phytoplankton, and animals. In Alaskan waters, these processes tend to proceed more slowly than at lower latitudes because of low ambient temperatures and low net incident solar radiation during much of the year. Thus, PAH introduced into Alaskan waters by natural mechanisms, intentional discharges, or accidental spills will tend to persist and may accumulate over time to high concentrations in Alaskan marine sediments.

Alaskan marine animals readily accumulate PAH and related hydrocarbons during exposure to these compounds in the water, food, or sediment. Bioaccumulation is most rapid and efficient from the water. However, since

PAH reach high concentrations and are more persistent in sediments than in water, the major source of PAH for benthic and demersal marine animals is from contaminated sediments.

Bioconcentration factors (concentration in tissues/concentration in medium) for PAH increase with increasing PAH molecular weight and tend to be higher in marine molluscs than in polychaetes, crustaceans, and fish. This is directly related to the relative capability of these taxa to metabolize and excrete PAH. Because PAH are metabolized by members of higher trophic levels, there is no evidence of biomagnification of PAH in marine food webs.

Low temperatures, characteristic of Alaskan waters, have only a slight effect on rate of accumulation of PAH in marine animals, but do seem to slow metabolic degradation and excretion of accumulated PAH. The slower rate of depuration plus the greater persistence of PAH in low temperature marine environments, may mean that the potential for chronic impacts of PAH pollution of the Alaskan marine environment is greater than for more temperate and tropical climates.

Alaskan marine animals do not appear to be significantly more sensitive to aromatic hydrocarbons than similar species from more temperate and tropical climates. However, because of the greater persistence of light aromatics and PAH in cold Alaskan waters, biological impacts of an Alaskan oil spill may be more severe and subsequent recovery slower than for a similar spill in a warmer climate. However, many marine communities in Alaskan coastal environments are already naturally stressed by the severe climatic conditions. Such communities recover rapidly following a disturbance such as an oil spill or cessation of a chronic pollutant discharge. The Alaskan marine populations most likely to be severely damaged by oil spills and chronic discharges are the large, long-lived species such as king crabs, salmon, and marine mammals.

Based on this review, we have made recommendations concerning additional information needs and the design of long-term monitoring programs. Specific information needs include: a quantitative inventory of PAH sources in the Alaskan marine environment; composition over time of produced water and ballast water discharges and their long-term fate after discharge to Alaskan coastal waters; sensitivity to and PAH metabolism by populations and communities of marine animals from the high arctic (Chukchi and Beaufort Seas); field validation of arctic oil spill models. The design of long-term monitoring studies to assess the environmental impacts of produced water discharges to Cook Inlet and of offshore oil and gas development in the Beaufort Sea were discussed.

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